Chemical Studies by Means of Molecular Beams. VIII.* A Method of Measuring the Intensity of Potassium Atomic Beams with an Incandescent Tungsten Surface. Part 2.

By Kumasaburo KODERA.

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Relation between the Surface Concentration of Adsorbed Atoms and the Ionization Efficiency. In the preceding report it was shown that the efficiency of ionization which was obtained by flashing the potassium atoms deposited on the tungsten surface differed considerably from what to be expected from the simple considerations as to the magnitudes of the work function and the contact potential of the tungsten used.

Now let us examine more closely the conditions of the tungsten surface and adsorbed potassium atoms. The tungsten ribbon was, as stated previously, heated to 1400–1500°C. This heat treatment is sufficient to get rid of the alkali contamination but not of the adsorbed oxygen, although it may completely eliminate the tungsten oxide. For the perfect removal of the adsorbed oxygen, the tungsten ribbon should be heated over 2900°K. In our experiments, therefore, we have always to do with a surface partly covered with oxygen, i.e. an incomplete W−O surface. The W−O surface has a very large electron work function, though its exact value has not yet been determined. Kingdon[1] takes the value to be about 9.2 V. and Reimann[2] about 6.2 V. and Bosworth and Rideal[3] about 6.3 V. At any rate in our experiments V_w must be valued at somewhat higher than 4.52 V.

Since our measurements indicate that the surface ionization curves show an appreciable departure from the linear course at $\theta = 0.04$, which corresponds to $x = \varepsilon(V_w - V_i - V_c)/kT = 2$, as we have already mentioned in the preceding report, we may estimate V_w if we know V_c, the contact potential of a potassium covered surface against the original surface. When potassium atoms are adsorbed on the W−O or W surface they are ionized there and adsorbed as ions, as long as θ is not too large. These adsorbed ions induce the negative charges under the metal surface and form the dipoles therewith. These dipoles produce the contact potential difference V_c according to the following equation:

$$V_c = 2\pi \sigma_0 \theta \mu , \qquad (1)$$

where $\sigma_0 = 3.56 \times 10^{14}$ is the number of atoms adsorbed per cm^2 of the true surface at $\theta = 1$ and μ is the average dipole moment. According

* Preceding papers were published in Japanese in the *J. Chem. Soc. Japan*, **57** (1936), **58** (1937).

(1) K. H. Kingdon, *Phys. Rev.*, **24** (1924), 510.

(2) A. L. Reimann, *Phil. Mag.*, **20** (1935), 594.

(3) R. C. L. Bosworth and E. K. Rideal, *Proc. Roy. Soc.* (London), A, **162** (1937), 1.

to de Boer[4] μ can be theoretically calculated by the equation:

$$\frac{\mu}{2} = \varepsilon r - \frac{\alpha \varepsilon}{(2r)^2}, \qquad (2)$$

where ε is the electronic charge and r the radius and α the polarizability of the potassium ion. Their values are respectively 4.8×10^{-10}, 1.33×10^{-8} and 0.88×10^{-24} and equation (2) gives then the value of μ to be

$$\mu = 11.36 \times 10^{-18} \text{ e. s. u.}$$

With this value of μ and $\theta = 0.04$, V_c is calculated from equation (1):

$$V_c = 300 \times 2\pi \times 3.56 \times 10^{14} \times 0.04 \times 11{\cdot}36 \times 10^{-18} = 0.305 \text{ V}.$$

As stated before, $V_w - V_i - V_c = 2kT/\varepsilon = 0.238$, when $\theta = 0.04$, so that $V_w - V_i = 0.543$ V or $V_w = 4.86$ V, since $V_i = 4.32$ V. On the other hand, Bosworth and Rideal[3] found the dipole moment of potassium on W − O surface at $\theta = 0.04$ to be 20.5×10^{-18} e. s. u. which gives $V_c = 0.55$ V, so that $V_w = 5.11$ V.

These latter values of V_c and V_w seem to be more reliable than the former, since they are based on the actual experimental data of μ, but there is no definite evidence for this. Accordingly, we shall continue our discussion taking both values into consideration. In equation (1) V_c is proportional to θ. In reality, however, as θ increases, the mutual depolarizing force of anions begins to be operative and gradually causes to slacken the increasing rate of V_c, so that the $V_c - \theta$ curve will pass a maximum and decrease to approach a constant value of solid potassium. Since in our experiments the value of θ is small, we may use equation (1) or

$$V_c = c\theta, \qquad (3)$$

where c is equal to $2\pi\sigma_0 \mu$ and found to be either 7.6 or 13.8, according as the theoretical or the experimental value of μ is used.

With either of these values and $T = 1379°$K for the ribbon temperature or $\varepsilon/kT = 8.4$ and $A = 0.111$ cm^2, the total ionization can be calculated numerically by means of equation (3) in the preceding report[5] from which ½ is omitted:

$$\nu_p = AN_0 \frac{kT}{c\varepsilon}\left[\log(1+\exp.[\varepsilon(V_w - V_i)kT] - \log(1+\exp.[\varepsilon(V_w - V_i - c\theta)/kT])\right]$$

The total ionization curves are shown in Figs. 1 and 2 with full lines. The experimental points represented by × and ⊙ correspond to those in Fig. 6 in the preceding report.

The agreement of the experimental points with the theoretical curves is not good in either case, but in the region of larger values of θ, it is better in Fig. 2 than in Fig. 1.

(4) J. H. de Boer, "Electron Emission and Adsorption Phenomena." 85, Cambridge (1935).

(5) K. Kodera, this Bulletin, **14** (1939), 114.

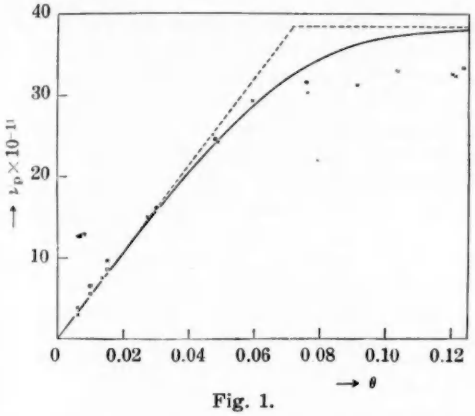


Fig. 1.

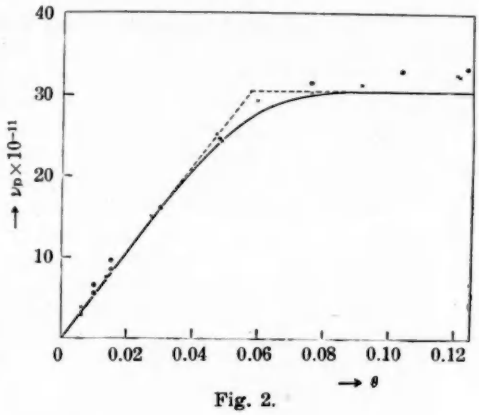


Fig. 2.

Now turning to our assumption $V_c = c\,\theta$, it must be noted that for larger values of θ this relation holds no longer good on account of the mutual depolarizing force. This argument makes plausible the deviation of the theoretical curves from the experimental points. It is therefore desirable to know a more precise relation between V_c and θ in this region of θ. Bosworth and Rideal[3] have determined μ for a wide range of θ, from which V_c is obtained as a function of θ (Fig. 3). With these values of V_c the differential ionization is calculated by equation (2) in the preceding report[5] with the factor ½ dropped:

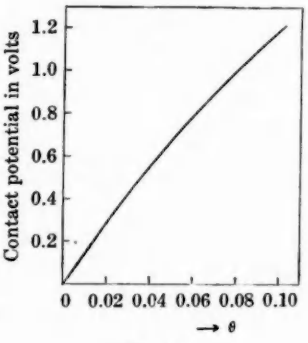


Fig. 3.

$$\frac{d\nu_p}{dN} = \frac{\exp.\,[\varepsilon(V_w - V_i - V_c)/kT]}{1+\exp.\,[\varepsilon(V_w - V_i - V_c)/kT]}$$

The results is shown in Fig. 4. The total ionization curve may be obtained from Fig. 4 by graphical integration. The result (Fig. 5) is seen to be in sufficient agreement with the experimental values.

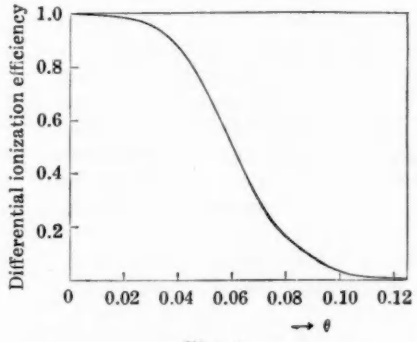


Fig. 4.

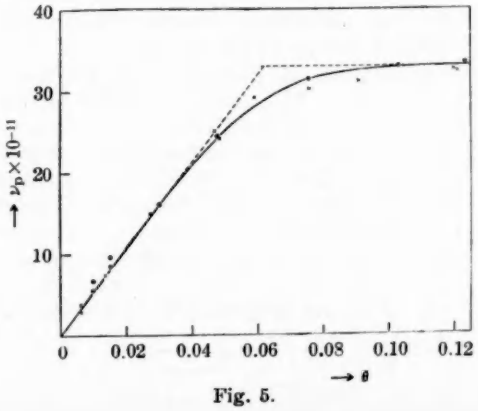


Fig. 5.

The Surface Migration of the Adsorbed Atoms. In our experiments, adsorbed atoms are at first confined to a very small portion of the ribbon surface. If the surface migration can take place, the site of the adsorbed atoms will gradually spread out and the surface concentration will accordingly become smaller. It must therefore be possible, by taking advantage of this phenomenon, to reduce a high surface concentration and bring about better or even complete ionization.

The phenomenon of surface migration is not significant when the ribbon is kept at room temperature but becomes noticeable at higher temperatures. (Bosworth and Rideal[3] have, however, reported that even at room temperature they observed the migration to occur when θ was large.) To examine this effect, deposits having a certain θ larger than 0.04 were preheated to 600–700°C. for different intervals of time, the cathode being kept at a higher potential to suppress the evaporation of ions. If the surface migration has occurred, the flashing should give a larger ion current than without preheating.

The results obtained in these experiments are shown in Figs. 6 and 7 in which the ordinate represents the galvanometer deflection and the

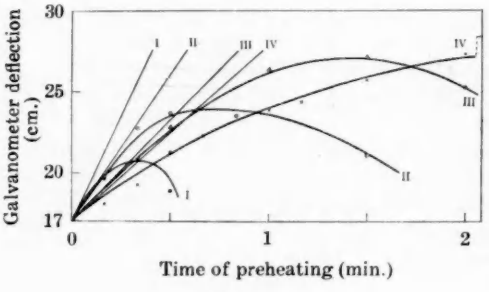


Fig. 6.

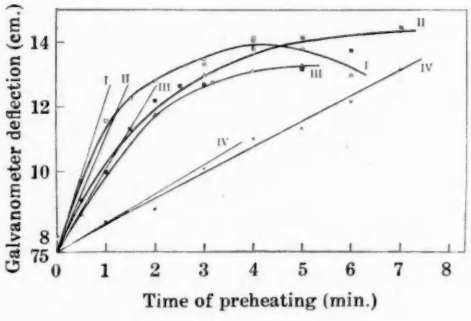


Fig. 7.

abscissa, the time of preheating. The existence of the surface migration is evident in all the curves. Curves I–IV in Fig. 6 were obtained respectively with the temperatures of 756, 704, 651 and 634°C. for preheating. Each of these curves has a maximum, the height of which decreases as the temperature of preheating rises. This is probably attributable to the fact that some fraction of the adsorbed atoms is evaporated while being preheated. That the rise of the curves is more rapid at a higher temperature of preheating is due to the greater migration velocity of the atoms. The dotted line in the figure represents the galvanometer deflection corresponding to the perfect ionization. The maximum of IV is equal to 94 per cent of that value. When the adsorbed atoms were heated at 580°C. for 6–7 minutes, a 100 per cent ionization was effected. In case θ was smaller than 0.04, the preheating caused no change in the ionization efficiency. This is self-evident since the ionization efficiency is 100 per cent from the outset.

This surface migration explains also the behaviour of curve II in Fig. 4 in the preceding report.[5] If a low flashing temperature of the

ribbon is effected with a small electric current, the rise of the ribbon temperature is comparatively slow, so that there is ample time for the surface migration to take place and improve the ionization efficiency in the region $\theta > 0.04$. But the migration velocity increases as temperature rises, so that, as exemplified in curve II, an optimum will be reached at a temperature where these opposing effects just balance. Making use of the surface migration, the portion of the linear increase in the initial part of the curve in Fig. 6 in the preceding report may be extended to the larger values of θ.

Energy of Activation of the Surface Migration. It would be interesting to correlate the preceding experimental results with the migration velocity of the adsorbed ions, although the experiments were not undertaken for this special purpose. Especially it should be mentioned that the data relating to the temperature are inexact, for the range with which we are here concerned lies outside the limit of direct measurement with an optical pyrometer.

Let us assume that the migration or diffusion coefficient of the potassium ion on the tungsten surface is a function of the temperature only and not of the surface concentration, although this assumption is only approximately right[6].

If a certain deposit of potassium atoms begins to expand at a certain temperature, the distribution of the surface concentration after a time t will be given by a function in which the diffusion coefficient D and the time t occur everywhere in the form of product Dt.

If then equal deposits simultaneously start the migration at different temperatures, they will attain the identical distribution of concentration successively in time t given by the relation $Dt = \text{constant}$. Although the total number of potassium atoms remains constant, every stage of expansion of the deposit is characterized by the corresponding amount of ions liberated upon flashing, since, as we have seen, the ionization efficiency is a function of the surface concentration. The same state of expansion to be attained at different temperatures may then be recognized by the equality of the galvanometer deflection obtained on flashing.

As to the actual determination of t from the curves in Figs. 6 and 7 use was made of the tangents drawn at the initial points with the purpose of avoiding the effect of the loss of potassium caused by evaporation during the preheating and of the change of contact potential with the surface concentration. The heat of activation Q for the migration may then be obtained from the inclination of the log $t-T^{-1}$ straight line, provided the diffusion constant is expressible in the form $Ae^{\frac{Q}{RT}}$

The value of Q was thus detemined for two cases of different initial surface concentrations $\theta = 0.10$ and 0.20 of the deposit. Q was found greater for the smaller surface concentration. The magnitudes of Q are fairly similar to those obtained by Bosworth,[6] who, by following the expansion of the deposit by the photoelectric activity, determined D for different temperatures and different surface concentrations and then Q

(6) R. C. L. Bosworth *Proc. Roy. Soc.* (London), A, **154** (1936), 112.

from the log $D-T^{-1}$ lines. Since, however, the probable error is large, it would be reasonable not to give our Q values but to associate to the curves the tangents whose relative inclinations were conversely determined from the value of Q as given by Bosworth, i.e. $Q = 0.59$ V. for $\theta = 0.10$; $Q = 0.53$ V. for $\theta = 0.20$. One will see in Figs. 6 and 7 that they are fairly in line with the curves.

Thus we see that the procedure we have just mentioned permits a convenient determination of the activation energy of surface migration though not the migration coefficient itself. Refined measurements would yield more accurate values.

Advantages of the Method of Flashing. This method of flashing with a tungsten ribbon has its own limit of application. If a measurement of the intensity at a point or along a line on the cross section of an atomic beam is required, it is more convenient to use a filament. On the contrary, for the measurement of the intensity of an atomic beam as a whole or of a very spacious portion of it, this method is preferable. One important precaution to be taken is to keep the specific surface concentration always below 0.04. Even if we take advantage of the surface migration, 0.1 would be the highest allowable surface concentration in practical use. For this reason, this method is more suitable for measuring weak atomic beams with a large cross section. An atomic beam of a high intensity can be measured with the ribbon kept at a flashing temperature, but this process generates much heat which may give rise to many troubles in the apparatus. Of atomic beams with the same total intensity, those with larger cross sections are more suitable for measuring than those with smaller cross sections.

An example will make this point clear. When a surface concentration of 0.04 is produced within a circle of radius 0.1 mm., the number of atoms adsorbed is:

$$4.8 \times 10^{14} \times 0.04 \times \pi\,(1 \times 10^{-2})^2 = 6.0 \times 10^{9}$$

where 4.8×10^{-14} is the number of atoms adsorbed on each cm^2. of the apparent area when θ is 1. The quantity of electricity to be obtained when all these atoms are ionized is:

$$1.6 \times 10^{-19} \times 6.0 \times 10^{9} = 0.96 \times 10^{-9} \quad \text{coulombs,}$$

where 1.6×10^{-19} is the charge of an ion in coulomb. By dividing this value by the sensitivity of the galvanometer used, 3.77×10^{-10} coulomb per 1 mm. deflection, the value of the galvanometer deflection is found to be

$$0.96 \times 10^{-9} / 3.77 \times 10^{-10} = 2.55 \text{ mm.}$$

Thus we see that the maximum allowable surface concentration within a circle of radius 0.1 mm. can give rise to only 2.5 mm. deflection of the galvanometer.

Summary.

In these experiments on the measurement of the intensity of potassium atomic beams with a tungsten ribbon, the following results have

been obtained:

(1) The ionization efficiency of adsorbed potassium atoms by flashing is found to be in good agreement with the calculated one, if the correct values of the work function and those of the contact potential of the tungsten surface are used.

(2) Adsorbed potassium atoms begin to migrate on the surface of the ribbon when the latter is heated to 500–700°C. This effect enables us to obtain a perfect ionization even with a concentration higher than $\theta = 0.04$.

(3) A simple method of determining the heat of activation of the surface migration is proposed.

From the above facts, it has been concluded that this method is the most suitable for measuring all at one time weak atomic beams of large cross sections.

The author expresses his sincere thanks to Prof. Nobuji Sasaki, at whose suggestion the present investigation has been undertaken. Thanks are also due to the Japan Society for the Promotion of Scientific Research for a grant to Prof. Sasaki, from which the expense has been defrayed.

Laboratory of Inorganic Chemistry,
Department of Science,
Kyo'o Imperial University.

Die kolloidchemische Untersuchung der Systeme von drei flüssigen Komponenten. III. Über Emulgierung zwei-flüssiger Systeme mit gleichen spezifischen Gewichte.

(Fortsetzung und Schluss.*)

Von **Naoyasu SATA** und **Haruhiko OKUYAMA.**

(Eingegangen am 13. März, 1939.)

(6) Über den Emulsionstyp und das Volumverhältnis. Das Verhalten der zwei-flüssigen Systeme gleicher spezifischen Gewichte nach dem Emulgieren, d. h. der Koagulationsverlauf, die Beständigkeit usw. wurden vorher erwähnt. Dahingegen tritt die Erscheinung der Emulgierung viel verwickelter auf, worauf wir weiter eingehend untersucht haben. Hierbei kommt der Emulsionstyp vorerst in Frage; nämlich, wie erwähnt, welche Flüssigkeitsschicht (W- oder NW-) dispergiert in die andere und bildet darin Emulsionströpfchen? Selbstverständlich hängt das Volumverhältnis beider Schichten unmittelbar damit zusammen. Zur Untersuchung dieser Fragestelle, haben wir einige Proben verschiedener

* Fortsetzung aus S. 139 dieses Bandes.

Volumverhältnissen hergestellt, welche in den Probiergläsern gleicher Grösse zugeschmolzen sind. Eine Serie dieser Proben wurde dann durch kräftiges Schütteln emulgiert und beobachtet. Den Emulsionstyp kann man nach einiger Übungen und Erfahrungen, einfach vom Aussehen der Emulsionen, leicht feststellen. Obwohl die W- und NW- Schicht von gleichem spezifischen Gewicht sind, unterscheiden sie sich voneinander in ihrer Brechungsvermögen, Viskositäten usw.. Deswegen lässt sich der Emulsionstyp, von dem Glanz der Tröpfchen oder der Mobilität des Systems, leicht erkennen. Die Versuchsergebnisse sind in Tabelle 3 zusammengestellt.

Tabelle 3.

Volum der W-Schicht (c.c.)	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5
Volum der NW-Schicht (c.c.)	4.5	4.0	3.5	3.0	2.5	2.0	1.5	1.0	0.5
Wasser-Benzol-Tetrachlorkohlenstoff	W/NW					NW/W			
Wasser-Amylalkohol (iso)-Chloroform	W/NW					NW/W			
Wasser-Methylalkohol-Benzol	W/NW		NW/W						

Daraus ersieht man, dass im allgemeinen eine Phase mit kleinerem Volum als disperse Phase, in die andere mit grösserem Volum dispergiert, wie von Wa. Ostwald[12] und anderen hingewiesen wurde. Aber beim Volumverhältnis in der Nähe 1:1, d. h., wo das System aus annähernd gleichem Volum disperser Phase und Dispersionsmittels besteht, merkt man, dass der Emulsionstyp, je nach den Komponenten des Systems, die charakteristische Tendenz vor sich zeigt. Nämlich das System A neigt sich mehr in W/NW- Typ zu emulgieren, während das System B und C die Tendenz haben, leichter NW/W-Typ zu ergeben.

(7) **Einfluss der Gasphase und der Gefässwand.** Durch oben ausgeführten Versuch wurde bestätigt, dass der Emulsionstyp eine charakteristische Tendenz vor sich zeigt, wenn das Volumverhältnis 1:1 annähert. An diesem Punkte wurde wiederum einen Versuch angestellt, unter besonderer Berücksichtigung der Gasphase und der Gefässwand.

Stamm und Kraemer[13] beschreiben dass wenn zwei unmischbare Flüssigkeiten umgerührt werden, treten zwei gegeneinander umgekehrte Erscheinungen auf. Namentlich einerseits, emulgiert sich eine Flüssigkeit in die andere und anderseits, koagulieren sich die entstandenen Tröpfchen durch Zusammenstösse. Sie nahmen an, dass dabei Volumverhältnis, Grenzflächenspannung, Viskosität usw. darüber massgebend sein. So haben sie experimentell bewiesen dass die Flüssigkeit höherer Viskosität die Tendenz hat, sich in die der niedrigerer Viskosität hinein zu emul-

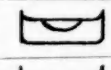
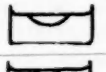
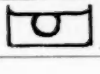
(12) Wa. Ostwald, *Kolloid-Z.*, **6** (1910), 103; **7** (1910), 64; **32** (1923), 77; **47** (1929), 131.

(13) A. J. Stamm und E. O. Kraemer, *J. Phys. Chem.*, **30** (1926), 992.

gieren und Tröpfchen bilden. Da sie den Versuch an den Systemen vom Wasser und Benzol, Nitrobenzol oder Tetrachlorkohlenstoff ausgeführt haben, lässt es sich vermuten, dass die Beobachtung nicht so einfach erzeugt war: denn die spezifische Gewichte der Komponenten waren so verschieden, dass die Trennung der Emulsion fast sofort nach dem Schütteln geschehen sein müsste. In unserem Falle wurde der Versuch, wegen Gleichheit des spezifischen Gewichtes, viel erleichtert. Ausserdem möchten wir noch darauf aufmerksam machen, dass man bei der Untersuchung der Emulgierungserscheinung mit gewöhnlicher Versuchsanordnung, den Einfluss der Gasphase und der Gefässwand nicht übersehen dürfen. Nämlich bei der Emulgierung, soweit sie in gewöhnlicher Weise durch mechanisches Schütteln oder Umrühren durchgeführt wird, ist es kaum möglich das Hineinmischen der Gasphase (Luft) in die flüssige Phase auszuschliessen. Ferner, ob die Flüssigkeit die Gefässwand benetzen oder nicht, könnte auch die Emulgierung beeinflussen.

Um die genannten Abhängigkeiten klar zu machen, haben wir folgendermassen versucht. Wir nahmen eine im Reagenzröhrchen zugeschmolzene Probe vom Volumverhältnis 1:1 und beobachteten genau den Einfluss obengenannter Faktoren auf Emulgierung bzw. Koagulierung. Die Resultate sind in Tabelle 4 zusammengestellt.

Tabelle 4.

Komponenten	Möglicher Emulsionstyp	Viskosität des Dispersionsmittels	Entstandene Emulsionstyp	Tröpfcheneigenschaften	Zustand an der Grenzfläche	
					Luft/L_1/L_2	Wand/L_1/L_2
Wasser—Benzol—	W/NW	0.75	W/NW	Klein und homogen		
Tetrachlorkohlenstoff	NW/W	1.00	—	Heterogen mit Luftbläschen		
Wasser—Amylalkohol-(iso)—	W/NW	2.03	W/NW	Klein und homogen		
Chloroform	NW/W	1.09	—	Heterogen mit Luftbläschen		
Wasser—Methylalkohol—	W/NW	2.76	—	Heterogen mit Luftbläschen		
Benzol	NW/W	1.29	NW/W	Klein und homogen		

Spalte 2und 3 zeigen die möglichen Emulsionstypen und die Viskosität des Dispersionsmittels entsprechendes Emulsionstyps.

Spalte 4 ergeben die beim Volumverhältnis 1:1 entstandenen Emulsionstypen.

In Spalte 5 wurde die Charakteristik der Emulsionströpfchen beschrieben. Selbstverständlich entsteht mit Volumverhältnis 1:1 nur ein Typ der Emulsion, wie in Spalte 4 ersichtlich ist. Aber durch Änderung des Volumverhältnisses könnte man auch einen anderen Typ erhalten. (Siehe Tabelle 3).

In Spalte 6 wurde die Stellung, welche ein Tröpfchen der dispersen Flüssigkeit (L_1) an der Grenzfläche zwischen Dispersionsmittel (L_2) und Luft genommen hat, skizziert. In anderen Worten, das Kennzeichen ist dargestellt, ob eine Flüssigkeit auf der Oberfläche der anderen sich verbreitet hat oder nicht. Natürlich ist es mit der Tröpfchengrösse abhängig. Die Abbildung gibt die Stellung eines Tröpfchens ähnlicher Grösse schematisch an.

In Spalte 7 sind die Grenzfläche beider Flüssigkeitsschichten gegen Gefässwand gezeichnet, welche mit der Benetzbarkeit der Flüssigkeiten zusammenhängen. Man sieht, dass der Grenzwinkel Wand/L_1/L_2 beim System A am kleinsten und beim C am grössten ist. Wenn man nun, die entstandenen Typen (Spalte 4) mit aderen Eigenschaften der Systeme-vergleicht, findet man interessante Tatsachen. Zuerst merkt man, dass zwischen der Viskosität (Spalte 3) oder dem Benetzungsproblem und entstandenem Type (Spalte 4) gar keine Abhängigkeit zu finden ist.

Dahingegen, die Tröpfcheneigenschaften und Grenzflächenzustände Luft/L_1/L_2 (Spalte 5 und 6) zeigen eine ausgesprochene Regelmässigkeit mit dem entstandenen Emulsionstyp. Es entsteht der W/NW-Typ aus System A bzw. B und NW/W-Typ aus System C. In diesen Fällen sind die Emulsionströpfchen gleichmässig in ihrer Grösse und haften gar keine Luftbläschen daran. Das einzelne Tröpfchen bleibt kugel-förmig auf der Oberfläche anderer Flüssigkeit und breitet sich nicht aus (siehe Spalte 6). Dahingegen sind die Tröpfchengrösse bei den nicht entstandenen Typen oder unbeständigen Typen ungleichmässig und man sieht dass feine Luftbläschen daran anhaften. Einzelnes Tröpfchen bleibt nicht kugel-förmig auf der Oberfläche des Dispersionsmittels, sondern es verbreitet sich linsen-förmig aus.

Wenn man sich hier daran erinnert, dass beim kräftigen Schütteln oder Umrühren unter gewöhnlichen Bedingungen, Hineinmischen der Luft (Gas-Phase) nicht zu vermeiden ist, könnte man folgendes schliessen. Da beim Schütteln, die flüssige Phase jedem Moment an erneuerte grosse Grenzfläche mit Luft begegnet,[14] die emulgierte Tröpfchen auf dieser Grenzfläche je nach ihren Eigenschaften, entweder linsen-förmig sich verbreiten oder unverändert kugel-förmig bleiben. Dann ist es, wie die Skizzen in Abb. 3 zeigen, leicht verständlich, dass die linsen-förmige Tröpfchen auf der Oberfläche viel leichter zu einer Flüssigkeitsmasse zusammenschmelzen als die kugel-förmigen, womit die Verschiedenheit der Beständigkeit zu erklären ist. Dass die Tröpfchen unbeständiger Emulsion die feinen Luftbläschen anhaften, scheint die Affinität zwischen Flüssigkeit und Luft zu tun haben, worüber noch eingehend untersucht werden müssen. Jedenfalls ist es dabei klar, dass diese Luftbläschen das scheinbare spezifische Gewicht der Tröpfchen vermindern, und sodann auch die Trennung der Emulsion beschleunigen können.

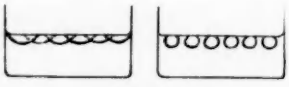


Abb. 3.

(8) **Über das Umrühren ohne Gasphase.** Wie erwähnt, beim Umrühren oder Schütteln, ist das Zusammenmischen der Gasphase gewöhn-

(14) A. von Buzagh, "Kolloidik," 282, Dresden und Leipzig (1936).

lich nicht vermeidlich. Aber die obenausgeführte Untersuchung hat uns gezeigt, dass das Verhalten der Tröpfchen auf der Oberfläche gegen Luft (Gasphase) eine wichtige Rolle über den Emulsionstyp und die Beständigkeit spielt. Jetzt ist es uns erwünscht die Emulgierungserscheinung zu untersuchen, welche nur zwischen zwei Flüssigkeiten geschieht und das Eintreten der Gasphase dabei vollkommen ausgeschlossen ist. Dazu nimmt man ein langes Reagenzglas (25 cm.) und füllt es mit gleichen Volumen beider Flüssigkeiten ein. Obwohl sie in ihrer spezifischen Gewichte gleich sind, bilden sie meistenfalls zwei flüssiges System mit der Grenzfläche in der Mitte. Das kommt vielleicht davon, weil die Benetzungsaffinität der beiden Flüssigkeiten gegen Gefässwand nicht ganz gleich ist. Man stellt dann einen Rührer an, welcher einigen cm. um die Flüssigkeitsgrenze auf und ab bewegt. Da die obere flüssige Schicht hoch genug ist, bleibt der Effekt des Rührens nur um die Flüssigkeitsgrenze herum, so dass das Hineinmischen der Luft ausgeschlossen ist. Die Vorrichtung ist schematisch in Abb. 4 ersichtlich. Der Versuch zeigt tatsächlich, dass die beiden Flüssigkeiten ohne Luftbläschen umgerührt werden. Dabei hat man keine Feststellung, welcher Emulsionstyp, d.h. entweder NW/W-Typ oder W/NW-Typ leichter zu entstehen ist. Hier scheint dass nur die mechanische oder hydrodynamische Bedingung des Rührens und höchstens die Viskosität damit zu tun haben.

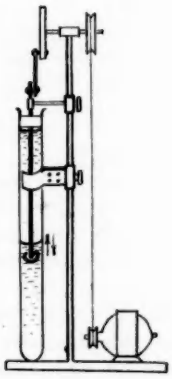


Abb. 4.

(9) **Über die Wirkung der USW.** Die emulgierende und koagulierende Wirkung der USW. an flüssig-flüssigen Systeme wurde von Söllner und Bondy[10] eingehend untersucht. Mit den Systemen der Flüssigkeitspaaren gleicher spezifischen Gewichte haben wir auch durchschnittlich ähnliches Resultat erhalten. Weil die Emulgierung durch USW. von der Grenzflächenzerstreuung und Kavitation hervorgerufen wird, entstehen dadurch die Emulsionen umgekehrter Typen in gleicher Zeit. Abb. 5 stellt das Verhalten schematisch dar. Bei der USW.-Emulgierung spielt

Abb. 5.

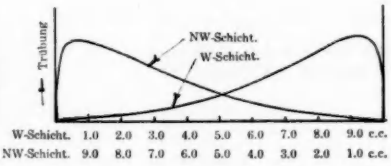


Abb. 6.

das Volumverhältnis wieder die wichtige Rolle. Und zwar der Versuch an Proben verschiedener Volumverhältnissen hat gezeigt, dass die Trübung der Flüssigkeitsschicht bei geeignetem Volumverhältnis einen Maximum ergibt. In Abb. 6 sind die Trübungskurven der W- und NW-Schicht mit

einem Maximum beim Volumverhältnis von etwa 1:9 übergetragen. Wir möchten hier darauf aufmerksam machen, dass die Erscheinung eine Art der Bodenkörperregel[15] zu betrachten ist. Nach Söllner und Bondy findet die USW.-Koagulation der Emulsionen im Bauche der stationären USW. statt, wenn die disperse Flüssigkeit leichter als Dispersionsmittel ist, wie z.B. Toluol im Wasser. Wohingegen, wenn das Gewichtsverhalten umgekehrt, wie Quecksilber im Wasser der Fall ist, geschieht die Koagulation im Knoten. Wie es mit unserem Fall von Flüssigkeitspaaren mit gleichen spezifischen Gewichte wird, soll eine interessante Aufgabe zukünftiger Untersuchung sein.

Zusammenfassung.

(1) Es wurde die Emulgierungserscheinung zwischen zwei Flüssigkeiten mit gleichen spezifischen Gewichte untersucht.

(2) Solche zwei-flüssige Systeme wurden hergestellt durch Kombinationen von drei Flüssigkeiten verschiedener Mischbarkeit und spezifischen Gewichte.

(3) Die Systeme „Benzol–Wasser–Tetrachlorkohlenstoff"; „Wasser–Amylalkohol (iso)–Chloroform" und „Wasser–Methylalkohol–Benzol" wurden untersucht. Sie ergeben bei geeigneter Konzentration zwei-flüssige Systeme, welche in spezifischen Gewichte gleich sind aber in Grenzflächenspannung usw. verschieden sind.

(4) Die Emulgierung und Koagulation sind trotz der Gleichheit der spezifischen Gewichte, noch von Grenzflächenspannung, Viskosität, Volumverhältnis abhängig.

(5) Ein Versuch mit besonderer Rücksicht an Emulsionstyp wurde ausgeführt, welcher bei Emulgierungserscheinung ausser obengenannten Faktoren eine wichtige Rolle spielt.

(6) Dadurch wurde festgestellt, dass man zum Emulgierungsproblem noch den Einfluss der Gasphase und Gefässwand in Betracht nehmen muss.

(7) Die USW.-Emulgierung ergab fast das gleiche Resultat wie in dem Falle des Systems des Flüssigkeitspaares nicht gleicher spezifischen Gewichte.

Chemisches Institut der Kaiserlichen
Universität zu Osaka.

(15) Wo. Ostwald, *Kolloid-Z.*, **43** (1927), 227, 249, 277.

Zur Mikrobestimmung des Selens in organischen Verbindungen.

Von Sumio UMEZAWA.

(Eingegangen am 20. März, 1939.)

Wrede[1] hat das Selen in organischen Verbindungen, wie bei der Schwefelbestimmung nach Pregl, unter Benutzung von Perlenrohr und Platinkontaktsternen bestimmt und dabei wurde die entstandene selenige Säure mit Alkali titriert. Enthält aber die Substanz Stickstoff oder Halogene, so ist die massanalytische Methode nicht ausführbar.

Danach haben Drew und Porter[2] die Substanz im Cariusröhrchen mit Salpetersäure oxydiert, die selenige Säure in salzsaurer Lösung mit Schwefeldioxyd reduziert, und das Selen in elementarer Form gewogen. Doch scheint hier, dass der Gebrauch konzentrierter Salpetersäure bei der Oxydation im Bombenröhrchen und die Fällung des Selens mit Schwefeldioxyd möglichst vermieden werden soll.

In vorliegender Mitteilung empfehle ich eine allgemein ausführbare Methode, die für die Selenbestimmungen von Halogen- und Nitroderivaten des Selenophens[3] und der Selenophthene[4] verwendet wird. Ich habe Spiralenrohr nach Pregl benutzt, die selenige Säure in stark salzsaurer Lösung mit Natriumsulfit reduziert, und das Selen gravimetrisch bestimmt.

Ausführung. Man verfährt im allgemeinen folgendermassen. Man wägt die Substanz, so dass sie 3–5 mg. Selen enthält.[5] Die Spirale[6] wird zuerst vor der Verbrennung mit reinem Wasser benetzt, um die selenige Säure aufzufangen. Die Platinkontaktsterne werden in den leeren Rohranteil eingeführt. Zuerst substituiert man die Luft im Rohre durch Sauerstoff in 3–5 Minuten und bringt dann die im Platinschiffchen abgewogene Substanz in das Rohr ein. Hierauf vollzieht man sehr langsam die Verbrennung im Sauerstoffstrom. (40–50 Blasen in 1 Minute).[7] Nach beendeter Verbrennung verlöscht man die Flammen und lässt im Sauerstoffstrom erkalten. Man entfernt den Kautschukstopfen und zieht das Schiffchen und die beiden Platinkontakte aus dem Rohre. Dann spannt man das Spiralenrohr unter einem spitzen Winkel gegen die Vertikale so ein, dass die Spitze des Spiralenrohres im Inneren des weiten Reagensglases[8] endet, und wäscht vorsichtig den Spiralenan-

(1) F. Wrede, *Z. physiol. Chem.*, **109** (1920), 272; H. Meyer, "Analyse und Konstitutionsermittlung organischer Verbindungen," V. Aufl., 205.

(2) H.D.K. Drew und C.R. Porter, *J. Chem. Soc.*, **1929**, 2091.

(3) H. Suginome und S. Umezawa, dies Bulletin, **11** (1936), 157; S. Umezawa, dies Bulletin, **11** (1936), 777.

(4) Noch nicht veröffentlicht.

(5) Für die Abwägung von flüchtigen Flüssigkeiten verwendet man Capillaren. Siehe F. Pregl, "Die quantitative organische Mikroanalyse," IV. Aufl., 62, (1935).

(6) Siehe F. Pregl, *loc. cit.*, 115.

(7) Verwendet wurde ein Blasenzähler von gleicher Grösse wie der von F. Pregl (*loc. cit.*, 26.) bei der Kohlenstoff-Wasserstoff-Bestimmung benutzte.

(8) F. Pregl, *loc. cit.*, 119.

teil mit destilliertem Wasser dreimal. Zu der gesammten Flüssigkeit von etwa 30 c.c. versetzt man 7 c.c. reiner konzentrierter Salzsäure und erhitzt 5 Minuten im siedenden Wasserbade. Zu der abgekühlten Lösung fügt man dann 3 c.c. gesättigte Natriumsulfitlösung[9] hinzu, wobei sich das Selen zuerst als amorphe rote Modifikation abscheidet. Durch Erhitzen aufs neue im siedenden Wasserbade während 30–40 Minuten ballt sich die schwarze Selenmodifikation und ist nach einstündigem Stehenlassen filtrierbar. Für die Filtration habe ich wie Drew und Porter das Filterröhrchen nach Pregl benutzt und sie mit Hilfe eines Hebers, ebenso wie bei der Halogenbestimmung nach Pregl, durchgeführt. Nach beendeter Filtration wäscht man das Innere des Filterröhrchens mit destilliertem Wasser und dann mit Alkohol dreimal. Nun wird im Regenerierungsblock 10 Minuten auf 105–110° getrocknet und nach Ablauf von 20 Minuten nach dem Abwischen gewogen.

Berechnung der Analyse: log % Se = log (gef. Selen) + (1–log Substanz)

Beispiele.

Nr.	Substanz in mg.			Gef. Se mg.	Gef. Se %	Fehler in %
1	Selenophen	C_4H_4Se	4.848	2.909	60.01	−0.27
2	Monochlorselenophen	C_4H_3ClSe	11.421	5.420	47.46	−0.25
3	Tetrabromselenophen	C_4Br_4Se	29.251	5.172	17.68	−0.04
4	β-Nitroselenophen	$C_4H_3O_2NSe$	8.895	4.008	45.06	+0.17
5	Monobromdinitroselenophen	$C_4HO_4N_2BrSe$	15.816	4.137	26.22	−0.15

Bei dem beschriebenen Verfahren ist es wichtig die Substanz, die 3–5 mg. Selen enthält, zu wägen. Die Anwesenheit von Halogenen oder Stickstoff (!) beeinträchtigt nicht dieses Verfahren.

Es sei mir erlaubt, Herrn Prof. H. Suginome für seine Ratschläge zu dieser Arbeit meinen herzlichen Dank auszusprechen.

Chemisches Institut
der Kaiserlichen Hokkaido-Universität,
Sapporo.

(9) Reines Präparat von Merck wurde verwendet.

Synthetische Versuche in der Selenophen-Gruppe. IV. Einführung von Seitenketten in den Selenophen-Kern.

Von Sumio UMEZAWA.

(Eingegangen am 20, März 1939.)

In den vorhergehenden Mitteilungen[1] wurden die Grund-Substitutionsreaktionen, die den Selenophenkern im allgemeinen als aromatisch kennzeichnen, mitgeteilt. Nun habe ich mich damit beschäftigt, Seitenketten in das Selenophen einzuführen.

Zu diesem Zwecke wurde zunächst die Fittigsche Synthese auf die Selenophen-Gruppe zu übertragen versucht, um womöglich zu den Selenophenhomologen zu gelangen, was aber bisher erfolglos blieb. Auch wurden die Halogen-selenophene[2], darunter auch das 2-Jodselenophen[3] mit Magnesium kaum grignardiert, auch wenn verschiedene Aktivierungsmethoden auf Magnesiumspäne angewendet wurden. Aus diesen Beobachtungen dürfte wenigstens geschlossen werden, dass diese grosse Reaktionsträgheit des Halogenatoms im Selenophen auf der eigentümlichen Struktur des letzteren beruht.

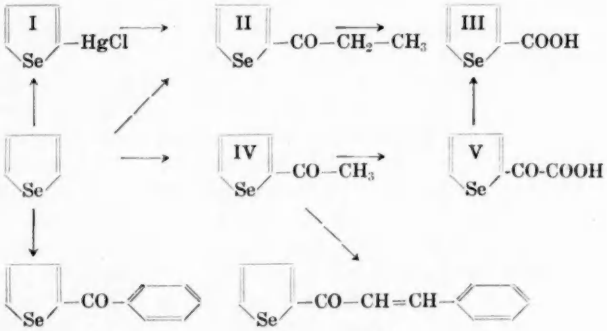
Infolge seiner besonderen Unbeständigkeit gegen Aluminiumchlorid bietet auch die Synthese nach Friedel-Crafts eine ausserordentliche Schwierigkeit, wobei das angewendete Selenophen sich gänzlich zersetzt. Doch gelingt die Darstellung der verschiedenen Selenenylketone mit mässiger Ausbeute, wenn man nach dem Prinzip der Stadnikoffschen Synthese[4] Zinntetrachlorid an Stelle von Aluminiumchlorid verwendet.

Besonders glatt verläuft die Kondensation zwischen aliphatischen Säurechloriden und Selenophen; lässt man Zinntetrachlorid in thiophenfreiem, wasserfreiem Benzol oder Schwefelkohlenstoff auf ein Gemisch von ebenso reinem Benzol oder Schwefelkohlenstoff, Selenophen und Acetylchlorid unter Kühlung einwirken, so kann man das α-Acetoselenenon (IV) vom Siedep. 107°/14.5 mm. erhalten, das mit Phenylhydrazin ein Phenylhydrazon vom Schmelzp. 116° ergibt. Kondensiert man das α-Acetoselenenon mit Benzaldehyd bei Gegenwart von Chlorwasserstoff, so bildet sich das 2-Cinnamoylselenophen (VII), d. h. Styryl-α-selenenylketon vom Schmelzp. 81–82.5°, welches das dem Chalkon entsprechende Selenophenderivat ist und durch Einwirken von Brom in das Dibromid C_6H_5·CHBr-CHBr-CO-C_4H_3Se vom Schmelzp. 155.5–156° übergeht. Beim Eintragen von Zinntetrachlorid in eine Benzol- oder Schwefelkohlenstofflösung von Propionsäurechlorid und Selenophen entsteht unter denselben Bedingungen ebenso das Propioselenenon (II) vom Siedep. 115°/14 mm., das ein Semicarbazon vom Schmelzp. 175–176° ergibt. Beachtenswert ist,

(1) Frühere Mitteilungen: dies Bulletin, **11** (1936), 157; **11** (1936), 775; **12** (1937), 4.
(2) H. Suginome und S. Umezawa, dies Bulletin, **11** (1936), 157.
(3) S. Umezawa, noch nicht veröffentlicht.
(4) G. Stadnikoff und W. Rakowsky, *Ber.*, **61** (1928), 268; Siehe auch *Ber.*, **61** (1928), 1996.

dass bei diesen Reaktionen, wie schon Stadnikoff[5] erwähnt hat, die Ausbeute an Selenenylketonen von den angewendeten Lösungsmitteln abhängt und beim Gebrauch von Benzol am grössten ist. Da es vorkommt, dass bei der Oxydation des Propioselenenons die später erwähnte α-Selenophensäure (III) am leichtesten zugänglich ist, so wurde die Reaktion zwischen α-Chlormercuri-selenophen (I) und Propionylchlorid versucht, um wenn möglich, die Ausbeute noch mehr zu erhöhen; doch ergab sich keine Verbesserung.

Die Kondensation des Selenophens mit Benzoylchlorid bei Gegenwart von Zinntetrachlorid in denselben Lösungsmitteln geht nicht so glatt wie bei der Darstellung der aliphatischen Selenenylketone; jedoch bildet sich dabei das Phenylselenenylketon (VI) vom Schmelzp. 57–8°, das auch ein Phenylhydrazon vom Schmelzp. 175–176.5° ergibt. Beim Erhitzen von Selenophen mit Benzoylchlorid und wenig Phosphorpentoxyd, das, wie schon Steinkopf[6] beobachtet, katalytisch einwirkt, entsteht auch das Phenylselenenylketon, allerdings mit geringer Ausbeute. Alle diese Ketone verhalten sich weit beständiger als das Selenophen selbst und geben Phenylhydrazon oder Semicarbazon als ihre funktionellen Derivate.



VI. VII.

Von diesen Ketonen, zumal von acetyliertem Selenophen, ist die grosse synthetische Bedeutung für die Selenophen-Gruppe, wie in der Thiophenreihe, zu erwarten, dass die Acetylierung ein bequemes Mittel bietet, kohlenstoffhaltige Seitenketten einzuführen, welche man dann in -COOH, -CO-COOH, -CHO, Alkylrest etc. verwandeln kann. Hier möchte ich über die Oxydation der Ketone berichten.

Oxydiert man das 2-Propionyl-selenophen mit stark verdünnter alkalischer Kaliumpermanganatlösung, so entsteht die α-Selenophensäure (III) vom Schmelzp. 122–124°, in einer ziemlichen Ausbeute. Die α-Selenophensäure ist in ihren Eigenschaften der Benzoesäure ähnlich und ergibt die Indophenin-Reaktion in ausgezeichneter Weise beim Erhitzen mit konzentrierter Schwefelsäure und Isatin.

(5) G. Stadnikoff und I. Goldfarb, *Ber.*, **61** (1928), 2341.
(6) W. Steinkopf, *Ann.*, **413** (1917), 343.

Auffallend ist, dass bei der Oxydation des Acetoselenenons mit verdünnter alkalischer Kaliumpermanganatlösung unter bestimmten Bedingungen fast einheitlich die α-Selenenylglyoxylsäure (V) vom Schmelzp. 92–94° ohne Nebenentstehung[7] der α-Selenophensäure erhalten wird. Lässt man die Säure aus wasserhaltigem Äther krystallisieren, so nimmt sie, wie bei der Glyoxylsäure, ein Molekül Wasser auf, das über Schwefelsäure oder Alkali im Vakuum leicht verloren wird; die wasserhaltige Selenenylglyoxylsäure schmilzt bei 44–46.5°. Ähnlich wie beim Chlorhydrat kann man auch bei Selenenylglyoxylsäure eine chemische Bindung von einem Molekül Wasser annehmen und so für dieselbe zur Strukturformel $C_4H_3Se{\cdot}C(OH)_2{\cdot}COOH$ einer Dioxyessigsäure gelangen, doch scheint die Formel $C_4H_3Se{\cdot}CO{\cdot}COOH + H_2O$ ausreichend zur Erklärung der Eigenschaften dieser Säure zu sein. Die α-Selenenylglyoxylsäure ist eine sehr starke Säure und ergibt das Semicarbazon vom Schmelzp. 192–193°, welches einen ziemlich starken Säurecharakter zeigt und aus seiner alkalischen Lösung durch Essigsäure in Gegenwart von überschüssigem Natriumacetat nicht oder nur unvollkommen gefällt wird, worüber Bougault[8] bei der Darstellung des Phenylglyoxylsäure-semicarbazons berichtet hat. Zur Darstellung des α-Selenenylglyoxylsäure-semicarbazons wurde die Ketosäure direkt mit Semicarbazidchlorhydrat, sogar in stark salzsaurer Lösung behandelt. Die α-Selenenylglyoxylsäure kann man weiterhin mit Wasserstoffsuperoxyd fast quantitativ in die α-Selenophensäure (III) verwandeln.

Ob die Substituenten in den verschiedenen Verbindungen tatsächlich die angegebene Stellung einnehmen, konnte nicht direkt bewiesen werden. Wenn man jedoch die grosse Ähnlichkeit[9] des Selenophens mit dem Thiophen in Betracht zieht, so erscheint der Analogieschluss erlaubt zu sein, dass sich die beiden Körper auch in Bezug auf die chemische Reaktionsweise übereinstimmend verhalten werden.

Herrn Prof. H. Suginome möchte ich an dieser Stelle für die Überlassung dieser Arbeit, sowie für Anregungen und Ratschläge meinen verbindlichsten Dank aussprechen. Gleichzeitig bin ich für die Gewährung eines Stipendiums der Kaiserlichen Akademie zu Dank verpflichtet.

Beschreibung der Versuche.

α-Acetoselenenon (α-Methylselenenylketon) (IV). Zu einer eisgekühlten Lösung von 6 c.c. Selenophen, 5.4 c.c. Acetylchlorid und 50 c.c. thiophenfreiem, gut getrocknetem Benzol tropft man eine Mischung von 8 c.c. Zinntetrachlorid in 10 c.c. ebenfalls reinem Benzol unter Umschütteln in Eiswasser ein. Das Reaktionsgemisch färbt sich sofort dunkelbraun. Man giesst es dann in Eiswasser, lässt es über Nacht stehen, um dabei entstandene Komplexverbindung zu zerlegen, äthert es aus und trocknet über Glaubersalz. Nach Eindampfen der Lösungsmittel unterwirft man das erhaltene braungefärbte Öl der Wasserdampfdestillation. Man äthert es wieder aus, trocknet über Glaubersalz, dampft ein und fraktioniert dann. Das α-Acetoselenenon ging als ein schwachgelbes stark lichtbrechendes Öl, bei 107°/14.5 mm. oder 103.5°/12 mm. über.

(7) Bei der Oxydation des Acetothienons entsteht als Nebenprodukt immer α-Thiophensäure. Siehe W. P. Bradley, *Ber.*, **19** (1886), 2115.

(8) J. Bougault, *Chem. Zentr.*, **1916**, II, 742; *J. pharm. chim.*, [7], **11**, 5.

(9) Siehe auch Umezawa, dies Bulletin, **12** (1937), 4.

Ausbeute 5 g., 42% der Theorie. d_4^{25}: 1.5530; n_D^{18}: 1.601. Gefunden: C, 41.47; H, 3.24; Se, 45.53. Berechnet für C_6H_6OSe: C, 41.61; H, 3.49; Se, 45.78%.

Wird eine Spur Acetoselenenon mit Isatin und Schwefelsäure erhitzt, so tritt die Indophenin-Reaktion in schöner Weise ein. Bei mässiger Oxydation in der Kälte wird es zu Selenenylglyoxylsäure oxydiert, wie später beschrieben ist.

α-Acetoselenenon-phenylhydrazon, $C_4H_3SeC(CH_3)=N\cdot NH\cdot C_6H_5$. Molekulare Mengen von Acetoselenenon, salzsaurem Phenylhydrazin und essigsaurem Natron werden in wässeriger Lösung zusammengebracht und öfters umgeschüttelt. An der Wand des Gefässes scheidet sich dann eine Krystallmasse ab. Aus Alkohol umkrystallisiert bildet das Acetoselenenon-phenylhydrazon hellgelb gefärbte, büschelförmig gruppierte Nädelchen vom Schmp. 114–116°. Gefunden: N, 10.76. Berechnet für $C_{12}H_{12}N_2Se$:N, 10.65%. Dies zersetzt sich vollständig nach einigen Wochen unter Bräunung.

α-Propioselenenon (II). Ein eisgekühltes Gemisch aus 3.9 c.c. Zinntetrachlorid und 4 c.c. thiophenfreiem, gut getrocknetem Benzol wird zu einem Gemisch aus 3 c.c. Selenophen, 3 c.c. Propionylchlorid und 30 c.c. ebenso reinem Benzol unter Umschütteln in Eiswasser nach und nach eingetragen. Das dunkelbraune Reaktionsgemisch wird sofort in Eiswasser gegossen, über Nacht stehen gelassen und wie beim α-Acetoselenenon aufgearbeitet. Das α-Propioselenenon siedet bei 115°/14 mm. und ist fast farblos. Ausbeute 2.3 g., 36% der Theorie. d_4^{25}: 1.4687; n_D^{14}: 1.587. Gefunden: C, 44.56; H, 4.01. Berechnet für C_7H_8OSe: C, 44.91; H, 4.31%.

α-Propioselenenon-semicarbazon, $C_4H_3SeC(C_2H_5)=N\cdot NH\cdot CO\cdot NH_2$. Das α-Propioselenenon wurde in wenig Alkohol gelöst und dazu einige Tropfen einer gesättigten wässerigen Lösung von gleichen Gewichtsteilen salzsaurem Semicarbazid und Kaliumacetat gegeben. Nach Stehen über Nacht wurde das auskrystallisierte Produkt aus wässerigem Alkohol umkrystallisiert. Farblose Fadenbüschel vom Schmp. 175–176°. Gefunden: N, 17.21. Berechnet für $C_8H_{11}N_3OSe$: N, 17.29%. Leicht löslich in Aceton, schwer löslich in Äther, auch in der Wärme; in Benzol löslich, unlöslich in Ligroin.

α-Chlormercuriselenophen (I). Die Darstellung der Quecksilberverbindungen von Selenophen wurde schon von Briscoe und seinen Mitarbeitern[10] untersucht. Das Monochlormercuriselenophen ist aber nocht nicht beschrieben.

Ein Gemisch von 3 c.c. Selenophen, 20 c.c. Alkohol und Natriumacetatlösung (10 g. Natriumacetat in 20 c.c. Wasser) wurde mit einer gesättigten Sublimatlösung (9.5 g. Sublimat in ungefähr 130 c.c. Wasser) versetzt. Das ganze Reaktionsgemisch wurde tüchtig über Nacht durchgeschüttelt, wobei ein weisser krystallinischer Niederschlag ausschied, der abfiltriert wurde. Das Filtrat lässt in der Regel bei längerem Stehen noch ziemlich viel des gleichen Niederschlags ausfallen. Nach dem Auswaschen mit kaltem Wasser wurde der Niederschlag mit reichlichen Mengen von Alkohol wiederholt ausgekocht, so lange die Lösung beim Erkalten noch Krystalle abschied. Die heisse alkoholische Lösung wurde mit dem Heisswassertrichter filtriert. Das α-Quecksilberchloridselenophen krystallisiert beim Erkalten in farblosen Tafeln, welche in der Flüssigkeit fast wie blankes Silber glänzen und nach dem Trocknen ein weisses Pulver darstellen. Es schmilzt bei 201–202° unter Aufschäumen. Ausbeute 7 g. Gefunden, Cl, 9.13. Berechnet für $C_4H_3ClSeHg$: Cl, 9.68%. Beim Aufbewahren färbt sich das α-Chlormercuriselenophen allmählich, und wird beim Dürchführen von Schwefelwasserstoff in alkoholischer Lösung zersetzt, wobei sich schwarzes Quecksilbersulfid niederschlägt.

Reaktion zwischen α-Chlormercuriselenophen und Propionylchlorid. 4.5 g. α-Quecksilberchloridselenophen wurden mit 1 c.c. Propionylchlorid gemischt und im Wasserbade am Rückflusskühler kurze Zeit erwärmt. Die Masse färbt sich anfangs fleischrot, dann schwarz. Nach dem Erkalten wurde das Reaktionsgemisch in Eiswasser gegossen und mit Natriumcarbonat neutralisiert. Nach Abfiltrierung des gelben Quecksilberoxyds wurde das Filtrat ausgeäthert und aufgearbeitet. Das nach dem Abdunsten des Äthers hinterbliebene braune Öl wurde mit Semicarbazid behandelt, wobei

(10) H.V.A. Briscoe, J. B. Peel und G.W. Young, *J. Chem. Soc.*, **1929**, 2589.

das Semicarbazon des α-Propioselenenons sich bildet, welches durch Mischprobe mit dem durch die Zinntetrachloridmethode erhaltenen Präparat festgestellt wurde.

α-Phenylselenenylketon (VI). Hier möchte ich bemerken, dass bei Verwendung von Schwefelkohlenstoff die Kondensation des Selenophens mit Benzoylchlorid bei Gegenwart von Zinntetrachlorid zu etwas besserer Ausbeute führt als bei Verwendung von Benzol als Lösungsmittel.

Zu einer Lösung von 2 c.c. Selenophen, 2.7 c.c. Benzoylchlorid und 20 c.c. Schwefelkohlenstoff wurden 2.6 c.c. Zinntetrachlorid in 5 c.c. Schwefelkohlenstoff unter Umschütteln in Eiswasser hinzugefügt, wobei die Reaktion nicht so heftig als bei der Kondensation des Acetylchlorids war. Das Aufarbeiten wurde wie bei der Darstellung des Acetoselenenons ausgeführt. Ausbeute 0.05 g. Umkrystallisiert aus Alkohol, schwach grünliche Nadeln vom Schmp. 57–58°. Gefunden: C, 55.93; H, 3.83. Berechnet für $C_{11}H_8OSe$: C, 56.17; H, 3.44%.

α-Phenylselenenylketon-phenylhydrazon, $C_4H_3SeC(C_6H_5)=N-NH-C_6H_5$. Das Phenylselenenylketon wurde in wenig Alkohol gelöst und dazu mit einigen Tropfen Phenylhydrazin erhitzt. Dann wurde die Lösung mit heissem Wasser verdünnt. Der ausgeschiedene Krystallbrei wurde abfiltriert und aus Alkohol umkrystallisiert. Schwach gelbe feine Nadeln, Schmp. 175–176.5°. Gefunden: N, 8.86. Berechnet für $C_{17}H_{14}N_2Se$: N, 8.62%.

Die Bildung von 2-Phenylselenenylketon aus Selenophen und Benzoylchlorid bei Gegenwart von wenig Phosphorpentoxyd. 1 c.c. Selenophen, 1.4 c.c. Benzoylchlorid und ungefähr 0.03 g. Phosphorpentoxyd wurden im Ölbade unter Rückfluss erhitzt. Bei etwa 90° (Bad) entwickelt sich Chlorwasserstoff sehr heftig und die Lösung färbt sich dunkelbraun. Die Reaktion wurde 15 Stunden lang bei etwa 100° fortgesetzt, bis die Chlorwasserstoffentwicklung praktisch aufgehört hatte. Das Reaktionsgemisch wurde in verdünnte Sodalösung eingebracht und ungefähr eine Stunde lang auf dem Wasserbade degeneriert. Ausgeäthert, Äther getrocknet, und verjagt. Rückstand war eine dickflüssige Masse, die beim Erkalten erst, wenigstens zum grössten Teile, erstarrte. Auf Ton gepresst, aus Alkohol umkrystallisiert. Schwach graue Nadeln vom Schmp. 57–58°. Mischschmelzpunkt stimmt mit dem durch Zinntetrachloridmethode erhaltenen Präparat überein. Die Ausbeute betrug 0.17 g., etwa 7% der Theorie.

2-Cinnamoylselenophen (Styryl-α-selenenylketon) (VII). Diese Verbindung wurde, analog der Claisenschen Darstellungsmethode[11] des Chalkons durch Kondensation von Acetoselenenon und Benzaldehyd auf folgende Weise gewonnen: Ein Gemisch von 2.5 c.c. Acetoselenenon und 1.6 c.c. Benzaldehyd war unter Abkühlung (ungefähr −10°) mit Salzsäure gesättigt und mehrere Tage sich selbst überlassen. Schon nach einigen Stunden wird die Flüssigkeit dunkel und syrupartig, um schliesslich zu einem unansehnlichen braunschwarzen Harz zu erstarren. Dieses wurde zur Entfernung der Salzsäure auf dem Wasserbade erwärmt und mit Ligroin unter Zusatz von Tierkohle mehrere Male extrahiert. Beim Einengen und dann Erkalten der Lösung erhält man schöne, schwachgelbe, gruppierte Prismen. Dreimal aus Ligroin umkrystallisiert, schwachgelbe gruppierte Prismen, Schmp. 81–82.5°. Gefunden: C, 59.93; H, 4.13. Berechnet für $C_{13}H_{10}OSe$: C, 59.75; H. 3.86%. Das 2-Cinnamoylselenophen ist in heissem Alkohol und Ligroin leicht löslich und ergibt kein Pikrat mit Pikrinsäure in Alkohol oder Äther.

Cinnamylselenenyl-dibromid, $C_4H_3Se-CO-CHBr-CHBr-C_6H_5$. Das Cinnamylselenenyl wurde in Schwefelkohlenstoff aufgelöst und zu der Lösung wurde eine Schwefelkohlenstofflösung von Brom nach und nach in etwas Überschuss zugesetzt. Nach ungefähr zehn Minuten wurden der Schwefelkohlenstoff und überschüssiges Brom in Vakuum über Paraffin und Alkali eingedunstet, wobei eine schwachgefärbte krystallinische Masse zurückblieb. Umkrystallisiert aus Alkohol unter Zusatz von Tierkohle. Rautenförmige Kryställchen. Schmp. 155.5–156°. Gefunden: Br, 38.25. Berechnet für $C_{13}H_{10}OBr_2Se$: Br, 37.97%.

(11) L. Claisen und A. Claperède, *Ber.*, **14** (1881), 2463.

α-Selenophensäure (Selenophencarbonsäure-(2)) (III). Zur Darstellung der Säure ist die Oxydation des α-Propionylselenophens am besten, welches vor der Acetylverbindung den Vorzug hat, dass bei der Oxydation die Säure direkt (ohne die Stufe der Selenenylglyoxylsäure) fast rein erhalten wird.

4.2 g. Kaliumpermanganat in 400 c.c. Wasser wurden zu einem Gemisch von 3 c.c. 50%ige Natronlauge in 230 c.c. Wasser und 2.4 c.c. Propioselenenon unter Umrühren im Laufe von 2 Stunden nach und nach eingetragen. Versuchstemperatur 20–24°. Das Reaktionsgemisch wurde dann vom Braunstein abfiltriert und bis auf ein kleines Volumen im Vakuum eingeengt. Säuert man dann die Lösung mit konzentrierter Salzsäure unter Abkühlung im Eiswasser, so scheidet sich die α-Selenophensäure in schwachbraun gefärbter krystallinischer Masse ab. Ausbeute 0.9 g., 41% der Theorie. Umkrystallisiert aus Wasser, schöne farblose Nadeln. Schmp. 122–124°. Gefunden: C, 34.28; H, 2.71. Berechnet für $C_5H_4O_2Se$: C, 34.30; H, 2.30%.

Die α-Selenophensäure ist in ihren Eigenschaften der Benzoesäure ähnlich. Mit Schwefelsäure und Isatin erhitzt, erzeugt sie eine schöne blaue Lösung.

α-Selenophensaures Silber, $C_4H_3Se{\cdot}COOAg$. Dieses wird in Form glänzender, durchsichtiger Blättchen erhalten, wenn man heisse verdünnte Lösungen von α-selenophensaurem Ammonium und Silbernitrat vermischt und erkalten lässt. Man filtriert es ab, wäscht mit kaltem Wasser und trocknet über Chlorcalzium im Vakuum. Gefunden: Ag, 38.27. Berechnet für $C_5H_3O_2AgSe$: Ag, 38.85%.

α-Selenenylglyoxylsäure (V). Man kann sie durch partielle Oxydation des Acetoselenenons rein erhalten. Man wendet am besten die folgenden Verhältnisse an. 2.5 c.c. Acetoselenenon werden mit einer Lösung von 6.7 g. Kaliumpermanganat und 1.6 g. Natriumhydroxyd in 530 c.c. Wasser in der Eiskühlung so lange tüchtig umgerührt, bis die anfangs rote, dann grüne Farbe der Lösung vollständig verschwunden ist, was ungefähr eine Stunde in Anspruch nimmt. Die alkalische Flüssigkeit wird von dem ausgeschiedenen Braunstein abfiltriert und das Filtrat wird unter Erwärmen im Vakuum eingeengt. Die hinlänglich abgedampfte Lösung wurde behufs Entfernung des unveränderten Acetoselenenons mit Äther einigemal ausgeschüttelt. Die ätherhaltige Lösung wurde sofort mit 2 N Salzsäure angesäuert und mit Äther bis zur Erschöpfung unter Zusatz von Kochsalz extrahiert. Der nach Eindampfen des Lösungsmittels gewonnene, ölige Rückstand krystallisiert nach kurzer Zeit bei der Abkühlung. Ist die Säure nur gut zwischen Filtrierpapier abgepresst worden, so schmilzt sie schon bei 42–45°. Ausbeute 1 g. Über Schwefelsäure, oder Alkali im Vakuum nimmt sie aber für einige Zeit einen fortwährend steigenden Schmelzpunkt an, und zwar liegt derselbe nach einem Tage bei ungefähr 85–90°. Umkrystallisierung zweimal aus Schwefelkohlenstoff, hellgelbe Prismen, Schmp. 92–94°.

Wasserbestimmung: Die getrocknete reine Säure wurde in wasserhaltigem Äther aufgelöst und bis zum Eindampfen stehen gelassen. Die auskrystallisierte Säure wurde auf Ton sorgfältig abgepresst; Schmp. 44–46.5°. Die wasserhaltige Säure wurde sofort gewogen und über Alkali—die Säure scheint über Schwefelsäure gefärbt—im Vakuum gestellt. Nach ungefähr 30 Stunden war Gewichtskonstanz eingetreten, und die Säure schmolz bei 92–94°. Gefunden: H_2O, 8.54. Berechnet für $C_5H_4O_3Se{\cdot}H_2O$, 8.15%. Gefunden: C, 35.35; H, 1.98. Berechnet für $C_5H_4O_2Se$: C, 35.55; H, 1.99%.

Die von Claisen[12] für Phenylglyoxylsäure angegebene, auf Zusatz von konz. Schwefelsäure und thiophenhaltigem Benzol entstehende Farbenreaktion ist undeutlich, da sich die Selenenylglyoxylsäure selbst in der konz. Schwefelsäure unter Färbung auflöst.

α-Selenenylglyoxylsäure-semicarbazon, $(C_4H_3Se){\cdot}C{:}(N{-}NH{-}CO{-}NH_2)COOH$. Das Semicarbazon der Selenenylglyoxylsäure besitzt einen hohen Schmelzpunkt und schmilzt unter Gasentwicklung. Er ist fast unlöslich in dem meisten organischen Lösungsmitteln und zeigt einen ziemlich starken Säurecharakter. Zur Darstellung dieses Semicarbazons wurde die α-Selenenylglyoxylsäure in wenig Wasser gelöst und dazu einige Tropfen einer gesättigten wässrigen Lösung von gleichen Gewichtsteilen salzsaurem Semicarbazid und Kaliumacetat gegeben. Da nach Stehen über Nacht kein

(12) L. Claisen, *Ber.*, **12** (1879), 1505.

krystallinischer Körper sich ausgeschieden hatte, setzte man einige Tropfen konzentrierter Salzsäure unter Eiskühlung zu. Das sofort ausgeschiedene α-Selenenylglyoxylsäure-semicarbazon wurde abgesaugt, mit Wasser sorgfältig gewaschen, getrocknet über Chlorcalzium im Vakuum und dann analysiert. Schmp. 192–193°, unter heftigem Aufschäumen und Bräunung. Gefunden: N, 15.81. Berechnet für $C_7H_7O_3N_3Se$: N, 16.16%.

α-Selenenylglyoxylsaures Barium, $C_7H_3SeCO\cdot COO\frac{1}{2}Ba\cdot\frac{1}{2}H_2O$. Die α-Selenenylglyoxylsäure wurde in wenig Wasser gelöst und mit Bariumcarbonat gesättigt. Die Lösung wurde von überschüssigem Bariumcarbonat abfiltriert und über Chlorcalzium im Vakuum eingedampft. Das ausgeschiedene Bariumsalz der α-Selenenylglyoxylsäure wurde aus Wasser umkrystallisiert. Gruppierte dünne Tafeln wurden über Chlorcalzium im Vakuum getrocknet und dann analysiert. Gefunden: H_2O, 2.97. Berechnet für $C_9H_3O_3Se\frac{1}{2}Ba\ \frac{1}{2}H_2O$: H_2O, 3.22%. Gefunden: Ba, 25.57. Berechnet für $C_9H_3O_3Se\frac{1}{2}Ba$: 25.37%.

Oxydation der α-Selenenylglyoxylsäure zur α-Selenophensäure. 0.3 g. α-Selenenylglyoxylsäure wurden in 4 c.c. Wasser aufgelöst und die Lösung wurde mit 5 Tröpfchen Perhydrol bei Zimmertemperatur versetzt, wobei fast keine Kohlendioxydentwicklung stattfand. Erhitzt man dann die Lösung bis auf 90°, so entfärbt sie sich und entwickelt heftig Konlendioxyd. Beim Erkalten der Lösung scheiden farblose Nadeln der Selenophensäure aus, die in kaltem Wasser wenig löslich sind. Ausbeute ist fast quantitativ. Sie wurden aus Wasser umkrystallisiert. Schmp. 122–124°. Mischschmelzpunkt mit dem authentische Präparat, das aus α-Propioselenenon erhalten wurde, zeigte keine Depression.

Chemisches Institut
der Kaiserlichen Hokkaido-Universität,
Sapporo.

Über die chemische Natur des Papains. III. Mitteilung.[1] Über die Wirkungsweise der Blausäure auf Papain.

Von Shigeo OKUMURA.

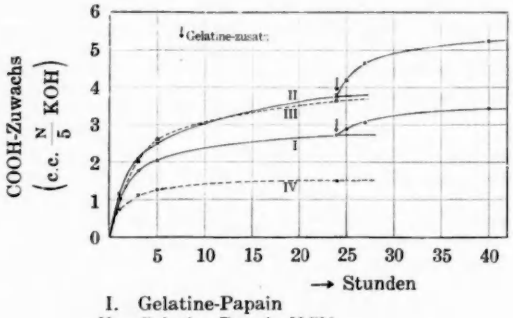
(Eingegangen am 28. März, 1939.)

In seiner II. Mitteilung[2] hat der Verfasser eine Reinigungsmethode des Papains mittels Taka-Amylase beschrieben und dabei erwähnt, dass bei dem so gewonnenen Papain-Präparat die SH-Reaktion mit Nitroprussidnatrium weder vor noch nach dem Behandeln mit Blausäure positiv verläuft, das Papain-Präparat aber durch Blausäure aktivierbar ist. Aus diesem Umstand hat der Verfasser abgeleitet, dass die Blausäureaktivierung des Papains nicht auf der Aufspaltung der in dem Enzymkomplex enthaltenen -S-S-Gruppen in SH-Gruppen, sondern auf der Entfernung des Hemmungskörpers beruht, der im Laufe der Verdauung entsteht oder im Papain-Präparat vorkommt.

(1) I. Mitteilung; dies Bulletin, **12** (1937), 319.
(2) dies Bulletin, **13** (1938), 534.

Auf Grund der oben erwähnten Tatsachen hat der Verfasser gemäss der vorliegenden Mitteilung Versuche über die Wirkungsweise der Blausäureaktivierung durchgeführt. Dabei wurde die Vorstellung des Verfassers über die Natur der Blausäure-Aktivierung durch den Befund, der in Abb. 1 und Tabelle 1 wiedergegeben ist, experimentell bestätigt. Es wurde nämlich, nachdem Gelatine durch ein mit Amylase gereinigtes Papain 24 Stunden lang verdaut worden war, abermals Gelatine zugesetzt. Dabei war der Anstieg der Verdauungskurve beim Papain-Gelatine-System (Kurve I) sehr gering, beim HCN-Papain–Gelatine–System (Kurve II) jedoch sehr deutlich.

Aus diesem Befund kann man den Schluss ziehen, dass das Papain beim HCN–Papain–Gelatine-System, da es infolge der Schutzwirkung der Blausäure vor eines Hemmungswirkung der Abbauprodukte behütet wird, die frisch zugesetzte Gelatine gut verdauen kann, während das Papain bei Abwesenheit von Blausäure durch Protein-Abbauprodukte gehemmt wird.



I. Gelatine-Papain
II. Gelatine-Papain-HCN
III. Gelatine-Gelatinepepton-Papain-HCN
IV. Gelatine-Gelatinepepton-Papain

Abb 1.

Um seine Annahme weiter zu verstärken, hat der Verfasser einen Versuch angestellt, bei dem er gefunden hat, dass das Papain beim Papain-Gelatine-System (Kurve IV) bereits von Anfang der Verdauung an stark, beim HCN–Papain–Gelatine-System (Kurve III) dagegen nicht gehemmt wird, wenn man das vorher hergestellte Protein-Abbauprodukt schon auf das Papain einwirken lässt, bevor dieses zur Gelatine gemischt wird. Demnach möchte der Verfasser annehmen, dass die Blausäureaktivierung des Papains nicht auf der Erweiterung der Spezifität, sondern auf der Beseitigung schädlichen Einflusses von Seiten des Hemmungskörpers beruht.

Der gleiche Hemmungseffekt auf Papain konnte man auch bei Glycyl-*l*-leucin beobachten. Die Hemmungswirkung dieses Peptides lässt sich gleichfalls durch Blausäur beseitigen (Tabelle 3). Dieser Befund legt die Vermutung nahe, dass der Hemmungskörper vielleicht ein spezielles Peptid sei. Zieht man die Tatsache in Beracht, dass das Papain ein eine Aldehyd-Gruppe tragendes Protein ist, wie der Verfasser schon in der I. Mitteilung mitgeteilt hat, so wird man zu dem Schluss kommen, dass

die Hemmungserscheinungen auf einer Schiffschen-Base-Bildung durch die Kondensation der Aldehyd-Gruppen des Papains mit den Amino-Gruppen der Peptide beruhe, und die Blausäureaktivierung daher ihren Grund in einer Behinderung dieser Kondensation und einer Regeneration der Aldehyd-Gruppen des Papains aus der bereits entstandenen Schiffsche-Base bestehe. Dieser Vorgang kann folgendermassen formuliert werden:

(I)

$$\underset{\text{aktives Papain}}{Pa{-}CHO} + \underset{\text{Hemmungskörper}}{H_2N{-}R} \xrightarrow{-H_2O} \underset{\substack{\text{inaktives Papain}\\ \text{(Schiffsche Base)}}}{Pa{-}CH{=}N{-}R} \quad \ldots\ldots\ldots \text{ Inaktivierung}$$

(II)

$$Pa{-}CH{=}N{-}R + HCN \longrightarrow Pa{-}\underset{\displaystyle CN}{\underset{|}{CH}}{-}NH{-}R \xrightarrow{+H_2O} Pa{-}\underset{\displaystyle CN}{\overset{\displaystyle OH}{\diagup\!\diagdown}}{CH} + H_2N{-}R \ldots \text{Aktivierung}$$

Schiffsche Base — Papain-Cyanhydrin

(III)

$$Pa{-}CHO + HCN \longrightarrow PaCH\underset{\displaystyle CN}{\overset{\displaystyle OH}{\diagup\!\diagdown}}$$

mehr aktiv — weniger aktiv

Nach der obigen Formulierung nimmt der Verfasser an, dass das Papain-Cyanhydrin mit Gelatine schwerer zu verbinden ist als das Papain, dass daher die Anfangsaktivität des Papain-Cyanhydrins niedriger, seine proteolytische Wirkung jedoch dauernder ist.

Über die Kondensation von Aldehyden mit Aminosäuren bzw. Peptiden sind Untersuchungen von Gerngross und Zühlke[3], Scheibler und Baumgarten[4] und Bergmann[5] angestellt worden. Die Aminosäuren bzw. Peptide werden nämlich schon durch Schütteln mit den Aldehyden in wässrigem alkalischem Medium leicht kondensiert. Z. B. entsteht aus Benzaldehyd und Glycin Benzyliden-Glycin.

$$C_6H_5CHO + H_2N{-}CH_2COOH = C_6H_5CH{=}NCH_2COOH + H_2O$$

Vor allem stellte M. Bergmann zahlreiche Aldehyd-Aminosäure-Verbindungen folgender Typen dar,

$$RCH{=}N{-}CHR'{\cdot}COOMe^{I} \qquad (RCH{=}NCHR'COO)_2Me^{II}$$

Me^{I} = einwertiges Metall oder Radikal
Me^{II} = zweiwertiges Metall

und erhielt die Ausgangsaminosäuren bzw. Peptide durch Spaltung mittels Mineralsäure wie Schwefelsäure, Salzsäure und Salpetersäure zurück.

Um den Wirkungsmechanismus der Blausäure zu prüfen, hat der Verfasser als Modellversuch das Benziliden-Glycin-Barium nach Angaben

(3) Gerngross, *Biochem. Z.*, **108** (1920), 89; Gerngross, Zühlke, *Ber.*, **57** (1924), 1482.
(4) Scheibler, Baumgarten, *Ber.*, **55** (1922), 1358.
(5) M. Bergmann, *Ber.*, **58** (1925), 1034; Bergmann, Zervas, *Z. Physiol. Chem.*, **152** (1926), 293, **172** (1927), 286.

von Bergman dargestellt und sowohl mittels 5N-Schwefelsäure als auch 20%ige Blausäure[6] aufgespalten. Dabei hat er beobachtet, dass das Benziliden-Glycin-Barium in Blausäurelösung leicht löslich und gleichzeitig unter Benzaldehyd-Abspaltung leicht zersetzlich ist.

Wenn der durch den Modellversuch dargestellte Vorgang wirklich stattfindet, dann liegt die Möglichkeit nahe, dass sich die durch Blausäure gespaltenen Hemmungskörper H_2N-R nach Schema (II) isolieren lassen soll, was sich experimentell leicht nachprüfen lässt. Nachdem das vorgereinigte[2] Papain in Wasser gelöst und mit Blausäure aktiviert worden ist, wird die Enzymlösung mittels Kollodiumhülse gegen destilliertes Wasser dialysiert. Aus der Aussenlösung der Dialyse wird durch Eindampfen im Vakuum eine dunkle braune Masse gewonnen, welche die Ninhydrin-Reaktion sehr deutlich zeigt und keine proteolytische Wirkung besitzt. Dabei ist es bemerkenswert, dass die Aktivität des Papains durch Beseitigung des Hemmungskörpers verstärkt wird. Wie in der Tabelle 4 ersichtlich ist, kann dieser dunkle braune Hemmungskörper die Wirkung des Papains hemmen, das letztere aber durch Zusatz der Blausäure reaktiviert werden.

Der Verfasser glaubt hiermit, dass, auf Grund der oben beschriebenen experimentellen Tatsachen, der Mechanismus der Blausäureaktivierung des Papains einigermassen geklärt worden sei.

Beschreibung der Versuche.

Versuchsreihe I. Zum Versuche wurde das mit Amylase gereinigte Papain angewandt. Ansätze: Nr. 1; 1%ige Papainlösung 10 c.c. (N-Acetatpuffer-Lösung ($pH = 5$)) + 5%ige Gelatine-Lösung 80 c.c. + Wasser 10 c.c. Nr. 2; 1%ige Papainlösung 10 c.c. + 5%ige Gelatine-Lösung 80 c.c. + 3%ige Blausäure-Lösung 10 c.c. Dann wurden nach einer bestimmten Zeitspanne 10 c.c. abpipettiert und deren Aktivität geprüft, nach 24 Stunden wieder 20 c.c. 5%ige Gelatine-Lösung zugesetzt, 12 c.c. abpipettiert und titriert. Nr. 3; 1%ige Papain-Lösung 5 c.c. + 5%ige Gelatine-Lösung 30 c.c. + Wasser 20 c.c. Nr. 4; 1%ige Papain-Lösung 5 c.c. + 5%ige Gelatine-Lösung 30 c.c. + Wasser 15 c.c. + 3%ige Blausäure 5 c.c. Nr. 5; 1%ige Papainlösung 5 c.c. + 5%ige Gelatine-Lösung 30 c.c. + 5%ige Gelatine-Pepton-Lösung 10 c.c. + Wasser 10 c.c. Nr. 6; 1%ige Papain-Lösung 5 c.c. + 5%ige Gelatine-Lösung 30 c.c. + 5%ige Gelatine-Pepton-Lösung 10 c.c. + 3%ige Blausäure-Lösung 5 c.c. + Wasser 5 c.c. Die Aktivität wurde mit jeweils 10 c.c. geprüft.

Tabelle 1. COOH-Zuwachs (c.c. N/5 KOH)

Stunde			1/6	1	3	5	24	Nachträgliche Zugabe von Gelatine		
								25	27	40
A	Nr. 1	ohne Zusatz	0.35	1.04	1.80	2.03	2.80	2.90	3.05	3.48
	Nr. 2	+HCH	0.32	1.15	2.10	2.55	3.75	4.20	4.70	5.30
B	Nr. 3	ohne Zusatz	0.28	1.14	1.66	2.00	2.71	—	—	—
	Nr. 4	+HCN	—	1.08	1.99	2.43	3.53	—	—	—
	Nr. 5	+Gelatine-Pepton	0.16	0.72	1.13	1.28	1.74	—	—	—
	Nr. 6	Nr. 5+HCN	—	1.04	2.03	2.51	3.65	—	—	—

(6) Gesättigte Lösung von gasförmiger Blausäure, die aus $Na_3Fe(CN)_6$ und H_2SO_4 entwickelt worden war.

Dieselbe Erscheinung wurde natürlich auch bei dem vorgereinigten Papain[2] beobachtet. Die Versuchsresultate sind in Tabelle 2 und 3 zusammengestellt.

Versuchsreihe II. Ansätze: Nr. 1; 5%ige Papain-Lösung (N-Acetat-Puffer-Lösung (pH = 5)) 5 c.c. + 5%ige Gelatine-Lösung 30 c.c. + Wasser 20 c.c. Nr. 2; 5%ige Papain-Lösung 5 c.c. + 5%ige Gelatine-Lösung 30 c.c. + 3%ige Blausäure-Lösung 5 c.c. + Wasser 15 c.c. Nr. 3; 5%ige Papain-Lösung 5 c.c. + 5%ige Gelatine-Lösung 30 c.c. + 4%ige Witte-Pepton-Lösung 10 c.c. + Wasser 10 c.c. Nr. 4; 5%ige Papain-Lösung 5 c.c. + 5%ige Gelatine-Lösung 30 c.c. + 4%ige Witte-Pepton-Lösung 10 c.c. + 3%ige Blausäure-Lösung 5 c.c. + Wasser 5 c.c. Nr. 5; 2.5%ige Papain-Lösung 5 c.c. + 5%ige Gelatine-Lösung 30 c.c. + Wasser 20 c.c. Nr. 6; 2.5%ige Papain-Lösung 5 c.c. + 5%ige Gelatine-Lösung 30 c.c. + Gelatine-Pepton-Lösung 10 c.c. + Wasser 10 c.c. Nr. 7; 2.5%ige Papain-Lösung 5 c.c. + 5%ige Gelatine-Lösung 30 c.c. + Gelatine-Pepton-Lösung 20 c.c. Die Aktivität wurde mit jeweils 10 c.c. geprüft.

Tabelle 2. COOH-Zuwachs (c.c. N/5 KOH)

Stunde			1	3	5	24
A	Nr. 1	ohne Zusatz	1.73	2.37	2.62	3.58
	Nr. 2	+HCN	2.05	2.87	3.20	4.63
	Nr. 3	+Witte-Pepton	1.59	2.10	2.20	2.67
	Nr. 4	+HCN+Witte-Pepton	2.48	3.58	4.10	6.20
B	Nr. 5	ohne Zusatz	1.33	1.70	1.92	2.26
	Nr. 6	+Gelatine-Pepton	0.96	1.20	1.28	1.70
	Nr. 7	+Gelatine-Pepton	0.90	1.06	1.10	1.42

Versuchsreihe III. Ansätze: Nr. 1; 2.5%ige Papain-Lösung (in N-Acetat-Puffer-Lösung (pH = 5)) 5 c.c. + 5%ige Gelatine-Lösung 30 c.c. + Wasser 20 c.c. Nr. 2; 2.5%ige Papain-Lösung 5 c.c. + 5%ige Gelatine-Lösung 30 c.c. + Glycyl-*l*-leucin 0.55 g. + Wasser 20 c.c. Nr. 3; 2.5%ige Papain-Lösung 5 c.c. + 5%ige Gelatine-Lösung 30 c.c. + Glycyl-*l*-leucin 1.1 g. + Wasser 10 c.c. Nr. 4; 5%ige Papain-Lösung 5 c.c. + 5%ige Gelatine-Lösung 40 c.c. + Wasser 10 c.c. Nr. 5; 5%ige Papain-Lösung 5 c.c + 5%ige Gelatine-Lösung 40 c.c. + 3%ige Blausäure-Lösung 5 c.c. + Wasser 5 c.c. Nr. 6; 5%ige Papain-Lösung 5 c.c. + 5%ige Gelatine-Lösung 40 c.c. + Wasser 10 c.c. + Glycyl-*l*-leucin 1.1 g. Nr. 7; 5%ige Papain-Lösung 5 c.c. + 5%ige Gelatine-Lösung 40 c.c. + 3%ige Blausäure-Lösung 5 c.c. + Wasser 10 c.c. + Glycyl-*l*-leucin 1.1 g. Die Aktivität wurde mit jeweils 10 c.c. geprüft.

Tabelle 3. COOH-Zuwachs (c.c. N/5 KOH)

Stunde			1	3	5	24
A	Nr. 1	ohne Zusatz	1.33	1.70	1.92	2.26
	Nr. 2	+Glycyl-*l*-leucin (0.1 g.)	1.06	1.49	1.58	1.98
	Nr. 3	+Glycyl-*l*-leucin (0.2 g.)	0.88	1.00 (2 Std.)	1.13 (4 Std.)	1.67
B	Nr. 4	ohne Zusatz	2.40	3.09	3.41	4.74
	Nr. 5	+HCN	2.37	3.41	3.95	5.78
	Nr. 6	+Glycyl-*l*-leucin (0.2 g.)	1.78	2.35	2.59	3.83
	Nr. 7	+Glycyl-*l*-leucin (0.2 g.)+HCN	2.10	2.86	3.40	5.58

Isolierung des Hemmungskörpers. Wenn das vorgereinigte Papain in Wasser gelöst, mit Blausäure 24 Stunden lang aktiviert und schliesslich 48 Stunden lang mittels Kolloidiumhülse gegen destilliertes Wasser dialysiert worden ist, wird die Aussen-Lösung im Vakuum engedampft und getrocknet. Die Innen-Lösung wird im Vakuum eingeengt und auf ihre Aktivität geprüft.

Tabelle 4. COOH-Zuwachs (c.c. N/5 KOH)

	Stunde		1/6	1	3	24
A	Nr. 1	Ausgangs-Enzymlösung	0.40	1.02	—	—
	Nr. 2	Innen-Lösung	0.68	1.40	—	—
	Nr. 3	Nr. 2+Hemmungskörper	0.54	1.12	—	—
B	Nr. 4	Innen Lösung	—	—	2.24	2.94
	Nr. 5	Nr. 4+Hemmungskörper	—	—	1.96	2.60
	Nr. 6	Nr 5+HCN	—	—	2.06	3.34

An dieser Stelle möchte ich Herrn Prof. S. Akabori für seine liebenswürdigen Ratschläge und freundliche Unterstützung meinen herzlichsten Dank aussprechen.

Chemisches Institut der Kaiserlichen Universität zu Osaka.

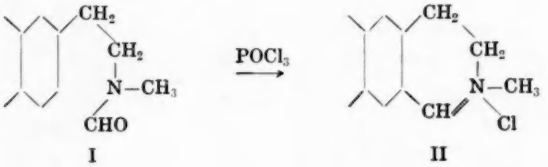
Über die Synthese aromatischer Aldehyde.

Von **Shiro AKABORI** und **Yoshinori SENOH.**

(Eingegangen am 28. März 1939.)

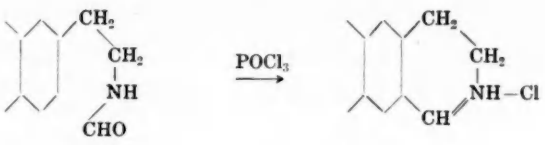
Die vorliegende Mitteilung beschreibt Versuche über eine neue, für Laboratoriumszwecke geeignete Synthese aromatischer Aldehyde.

Vor dreizehn Jahren hat der eine der Verfasser (S. Akabori)[1] gefunden, dass die bei der Kondensation von Formyl-phenyläthylaminderivaten zu 3,4-Dihydroisochinoliniumsalzen (II) mittels Phosphoroxychlorid viel bessere Ausbeuten der Formyl-*N*-methylphenyläthylaminderivate (I) gaben als die der Formylderivate (III), bei denen die Methylgruppe fehlt.



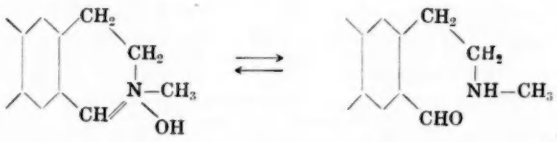
I II

(1) dies Bulletin, **1** (1926), 96.



III

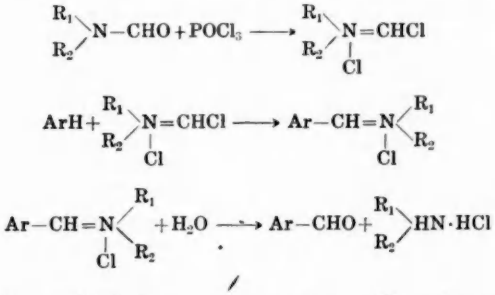
Für die freie Base von *N*-Methyl-3,4-dihydroisochinolin liegt ein Gleichgewicht wie folgt vor:



deswegen reagiert sie wie ein Aldehyd, indem sie nämlich leicht mit Hydroxylamin zum Oxim kondensiert.

Demnach ist die oben erwähnte inneremolekulare Kondensation von Formyl-*N*-methyl-phenyläthylamin zum Dihydro-isochinoliniumsalz und darauffolgende Hydrolyse nichts anderes als die Umkettung der mit dem Stickstoff verknüpften Formylgruppe an den Benzolkern.

Wenn sich eine derartige Kondensation zwischenmolekular erzielen lässt, so ist wohl durch Hydrolyse des Kondensationsprodukts Aldehyd zu gewinnen. In der Tat ist uns die Synthese einiger aromatischer Aldehyde nach dem obigen Prinzip gelungen. Wir konnten aus Anisol und Formylpiperidin Anisaldehyd, aus Veratrol und Formylpiperidin Veratrumaldehyd und aus Resorcin-dimethyläther und Formyldiäthylamin Resorcylaldehyd-dimethyläther darstellen. Der Reaktionsmechanismus lässt sich wohl durch folgende Reaktionsreihe wiedergeben.



Als Kondensationsmittel kann man ausser Phosphoroxychlorid auch Phosphortrichlorid benutzen.

Eine ganz ähnliche Synthese aromatischer Aldehyde mittels Formylanilin wurde schon von Dimroth und Zoeppritz[2] beschrieben. Diese Synthese lässt sich aber nur bei Phenolen, die leicht am Kern substituierbar sind, wie Resorcin oder Pyrogallol anwenden, nicht aber bei Phenol-

(2) *Ber.*, **35** (1902), 993.

äthern. Unsere Methode ist dagegen für Phenoläther geeignet, aber nicht für Phenole.

Beschreibung der Versuche.

Anisaldehyd aus Anisol und Formylpiperidin. 10 g. Formylpiperidin und 20 g. Anisol wurden in einem Rundkolben zusammengegossen und zu dem Gemisch unter Eiskühlung 10 g. Phosphoroxychlorid langsam hinzugefügt. Das Reaktionsgemisch wurde 12 Stunden lang bei Zimmertemperatur stehen gelassen und dann 6 Stunden auf dem Wasserbad erhitzt, wobei sich die Masse intensiv gelb färbte. Nachdem sie abgekühlt worden war, wurde eine grössere Menge Petroläther zugefügt um das überschüssige Anisol aufzunehmen. Das am Boden des Kolbens ausgeschiedene Reaktionsprodukt wurde von dem Petroläther getrennt und langsam mit eiskaltem Wasser versetzt. Die Hydrolyse fand sofort statt und die Ausscheidung von Anisaldehyd machte sich durch dessen Geruch bemerkbar. Der Aldehyd wurde mit Äther ausgeschüttelt, die ätherische Lösung mit wasserfreiem Natriumsulfat getrocknet und der Äther abdestilliert. Das zurückbleibende Öl wurde unter vermindertem Druck destilliert. Die Fraktion, die bei 130–140°/35 mm. überging, erweis sich als Anisaldehyd. Ausbeute 3.5 g. (21% der Theorie).

Das Kondensationsprodukt mit Dimethylbarbitursäure schmolz bei 147–148° (Nach Akabori[3] schmilzt Anisal-dimethylbarbitursäure bei 147–148°). (Gef.: N, 10.23. Ber. für $C_{14}H_{14}N_2O_4$: N, 10.21%).

Veratrumaldehyd aus Veratrol und Formylpiperidin. 15 g. Veratrol, 8 g. Formylpiperidin und 13 g. Phosphoroxychlorid wurden unter Eiskühlung vermischt, bei Zimmertemperatur über Nacht stehen gelassen und dann 8 Stunden auf den siedenden Wasserbad erhitzt. Das so gewonnene Kondensationsprodukt wurde mit eiskaltem Wasser versetzt und mit Äther ausgezogen. Die ätherische Lösung wurde mit Natriumbisulfit-Lösung geschüttelt um den Aldehyd in die wässrige Schicht überzuführen. Letztere wurde mit Natriumcarbonat versetzt und wieder mit Äther ausgezogen. Die ätherische Lösung wurde dann mit Natriumsulfat getrocknet, der Äther abdestilliert und das zurückbleibende Öl unter vermindertem Druck destilliert. Die bei 171–173°/21 mm. übergegangene Fraktion wurde aus Ligroin umkrystallisiert. Schmp. 45°. Ausbeute 5.0 g. (33% der Theorie).

Zur Identifizierung wurde Veratrumaldehyd-semicarbazon dargestellt, das bei 179.5° schmolz. (Gef.: N, 18.94. Ber. für $C_{10}H_{13}N_3O_3$: N, 18.84%).

Resorcylaldehyd-dimethyläther aus Resorcin-dimethyläther und Formyldiäthylamin. Das Gemisch von 15 g. Resorcin-dimethyläther und 8 g. Formyldiäthylamin wurde unter Eiskühlung mit 12 g. Phosphortrichlorid versetzt, bei Zimmertemperatur über Nacht stehen gelassen und dann auf dem Wasserbad 8 Stunden lang erhitzt. Das Reaktionsgemisch wurde genau so wie bei der Synthese von Veratrumaldehyd weiter verarbeitet. Das aus 95%igem Alkohol umkrystallisierte Produkt schmolz bei 71°. Ausbeute 7 g. (40% der Theorie).

Das Oxim aus dem nach oben synthetisierten Resorcylaldehyd-dimethyläther-schmolz bei 103–104°. (Gef.: N, 7.44. Ber. für $C_9H_{11}NO_3$: N, 7.74%).

Chemisches Institut der kaiserlichen Universität zu Osaka.

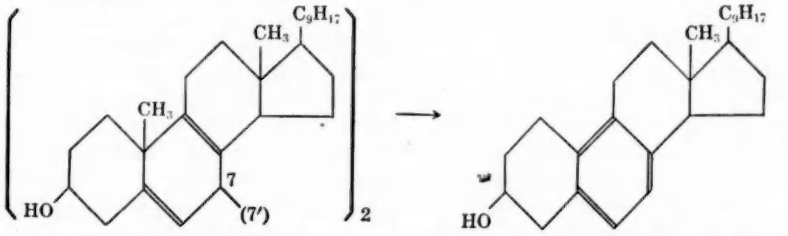
(3) *Ber.*, **66** (1933), 139.

Iso-dehydroergosterol as A Component of Iso-neoergosterol, A Molecular Compound Obtained from the Pyrolysis of Ergopinacone.

By Toshio ANDO.

(Received March 29, 1939.)

Ergosterol, $C_{28}H_{44}O$, as found by Windaus and Borgeaud,[1] undergoes dehydrogenation when its alcoholic solution containing eosin is exposed to light in the absence of oxygen. The product, $C_{56}H_{86}O_2$, has been unappropriately called ergopinacone. Ergopinacone suffers a characteristic decomposition on submitting it to distillation in vacuum or on heating it with acetic anhydride.[2] In this decomposition methane is eliminated, and neoergosterol, $C_{27}H_{40}O$, has been the only other fragment to be characterized, although Inhoffen[3] suggested that ergopinacone and its decomposition might be formulated as follows:



(I) Ergopinacone, $C_{56}H_{86}O_2$. (II) Neoergosterol, $C_{27}H_{40}O$.

$+ CH_4 + (C_{28}H_{42}O\,?)$.

Some time ago Urushibara and the present author[4] obtained a new compound besides neoergosterol from the pyrolysis followed by distillation in vacuum of ergopinacone, and named it iso-neoergosterol, since it then appeared to be an isomeride of neoergosterol. Subsequently,[5] on acylation with 3,5-dinitrobenzoyl chloride and pyridine it gave equal quantities of two different dinitrobenzoates, one being neoergosteryl 3,5-dinitrobenzoate melting at 227–228° (corr.) with decomposition and the other a 3,5-dinitrobenzoate with the presumable composition $C_{35}H_{44}O_6N_2$ melting at 187.5°–189.5° (corr.) with decomposition. The latter corresponded in composition to the dinitrobenzoate of a compound with the formula $C_{28}H_{42}O$. However, the dinitrobenzoate was not identical with dehydroergosteryl dinitrobenzoate with the same composition and the same melting point. Thus the author was led to presume that iso-neoergosterol was a

(1) A. Windaus and P. Borgeaud, *Ann.*, **460** (1928), 235.
(2) H. H. Inhoffen, *Ann.*, **497** (1932), 130.
(3) H. H. Inhoffen, *Naturwissenschaften*, **25** (1937), 125.
(4) Y. Urushibara and T. Ando, this Bulletin, **11** (1936), 757.
(5) T. Ando, *ibid.*, **13** (1938), 371.

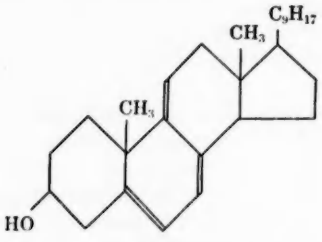
molecular compound of neoergosterol and an isomeride of dehydroergosterol. The latter component has now been isolated in free state. The author proposes the name "iso-dehydroergosterol" for this new sterol derivative, because it is most probably an isomeride of dehydroergosterol.

Careful hydrolysis of the 3,5-dinitrobenzoate melting at 187.5–189.5° with 1% alcoholic potash and recrystallization of the product from methanol gave free iso-dehydroergosterol in colourless aggregated needles with a melting point 128–129.5° (corr.) and a specific rotation $[\alpha]_D^{10°} = -102°$ in chloroform. The substance is easily soluble in organic solvents, and gives instantly an insoluble addition compound with digitonin. It is thus shown that iso-neoergosterol owes its pronounced precipitability with digitonin to this component.

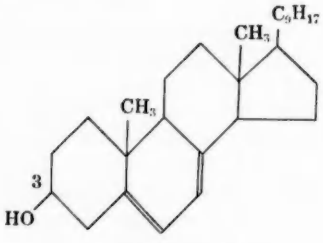
On account of great difficulty in drying completely the substance due to unstability to heat and of the hygroscopic nature of the dried substance, analyses gave no satisfactory results. However, it was possible to decide between two alternative formulas, $C_{28}H_{44}O$ and $C_{28}H_{42}O$: By taking advantage of the fact that the hydrogen content is hardly affected by the addition of water (H_2O requires H = 11.19%) to the ergosterol formula ($C_{28}H_{44}O$ requires H = 11.19%) and of a molecule or a fraction of water to the dehydroergosterol formula ($C_{28}H_{42}O$ requires H = 10.74 and $C_{28}H_{42}O+H_2O$ H = 10.75%), it could be shown that the dehydroergosterol formula is preferable to the ergosterol formula (Found: H = 10.96, 10.85%). The analyses of the dinitrobenzoate also corresponded to the dehydroergosterol formula more satisfactorily than to the ergosterol formula.[5] Lack of the material made it unable to determine the number of double bonds by any other method.

Iso-dehydroergosterol is not stable in air nor to heat, gives distinctly the colour reactions of Liebermann-Burchard and of Rosenheim, and shows sharp absorption maxima at 280, 270 mμ, and indistinct one at 252 mμ.[6]

Comparison of the free alcohols also indicates clearly that iso-dehydroergosterol is different from dehydroergosterol (III). The latter melts at 146° and gives $[\alpha]_D^{18°} = +149°$ and an absorption maximum at 320 mμ corresponding to the three conjugate double bonds.[7]



(III) Dehydroergosterol.



(IV) Ergosterol.

(6) The author thanks Dr. K. Yamasaki for taking absorption spectra.
(7) A. Windaus and O. Linsert, *Ann.*, **465** (1928), 148.

As for the constitution of iso-dehydroergosterol, its properties as described above indicates that a hydroxyl group is situated at carbon atom 3 with the same configuration as in ergosterol (IV), and further may suggest that, of the three dobule bonds in the ring system, two are conjugated probably in one ring and another is isolated in one of the other rings. However, it is hardly possible to infer the positions or the distribution of these three double bonds from the data of absorption spectra, rotatory power, and colour reactions, because there are no sufficient materials to formulate any rules for compounds with three double bonds in the ring system. Even if Inhoffen's formula (I) for ergopinacone is assumed, it would give no reference for knowing the positions of the double bonds in the product from such a destructive change as pyrolysis.

Iso-neoergosterol can be synthesized from components: When neoergosterol and iso-dehydroergosterol in equal quantities were dissolved in and crystallized from acetone, the molecular compound separated out. Recrystallization gave colourless needles melting at 138–139° (corr.) alone and in admixture with the specimen obtained from the pyrolysis of ergopinacone. The synthetic compound showed a specific rotation $[\alpha]_D^{11°} = -66.1°$ while the other $[\alpha]_D^{29°} = -59.1°$.[5] The synthetic iso-neoergosterol, as a molecular compound, showed a depression in the melting point when mixed with a small amount of either component.

The isolation of iso-dehydroergosterol, $C_{28}H_{42}O$, from the pyrolysis of ergopinacone substantiates Inhoffen's hypothetical equation for this reaction. On recrystallizing the crude product from this reaction neoergosterol crystallizes out first, and then iso-neoergosterol follows. Iso-neoergosterol is the molecular compound of neoergosterol and iso-dehydroergosterol, but cannot be separated into components by mere recrystallization. Hence, it is clear that in this reaction more neoergosterol is formed than iso-dehydroergosterol, while Inhoffen's equation requires equimolecular amounts of neoergosterol and a compound or a group of compounds with the formula $C_{28}H_{42}O$. It seems, therefore, that iso-dehydroergosterol either is formed by a secondary change from the direct product of the pyrolysis or suffers partly a transformation during distillation. Or otherwise, a number of compounds with the formula $C_{28}H_{42}O$ may be formed side by side. In any case, at least one more compound with the formula $C_{28}H_{42}O$ may be expected, unless the primary product suffers such a change as to alter its composition.

Experimental.

The Isolation of Iso-dehydroergosterol. Iso-dehydroergosteryl 3,5-dinitrobenzoate was obtained from iso-neoergosterol in the same way as described in the previous paper.[5] For the experiments recorded in this paper 87 mg. of a specimen of the dinitrobenzoate melting at 187–189.5° (corr.) and 91 mg. of another melting at 184.5–187° (corr.) were available. The dinitrobenzoate was carefully saponified as follows:

The dinitrobenzoate (87 mg.) of the melting point 187–189.5° was dissolved in benzene (14 c.c.), and the solution was added drop by drop to boiling 1% alcoholic potash (0.06 g. potassium hydroxide in 6 g. alcohol), while the benzene was instantly distilled off. The resulting brown solution was concentrated under a slightly diminished pressure and water was added to the concentrate, when a dark brown viscous matter separated. It was extracted with ether, and the ethereal solution was washed with dilute acetic acid and with water, dried with anhydrous sodium

sulphate, and evaporated. The remaining orange-coloured mass, after dried over caustic potash in vacuum, was crystallized from hot methanol in almost colourless needles (46 mg.) melting at 130–131.5° (corr.). Repeated recrystallization from methanol containing a small amount of water gave pure iso-dehydroergosterol in colourless aggregated small needles (21 mg.). It melts at 126.5–128° (uncorr.) or 128–129.5° (corr.) to a colourless liquid, and shows $[\alpha]_D^{16°} = -102°$ (7.35 mg. in 1 c.c. chloroform solution, $l = 1$ dm., $\alpha_D^{16°} = -0.75°$) and ultraviolet absorption maxima in 0.036% hexane solution at 280, 270 (both sharp), and 252 mμ (indistinct). An additional yield (9 mg.) was obtained from the mother liquors of recrystallization.

In the same way the other specimen (91 mg.) of the dinitrobenzoate melting at 184.5–187° gave another crop of iso-dehydroergosterol (35 mg.) in colourless aggregated small needles showing melting point 125.5–128° (uncorr.) or 127–129.5° (corr.), and ultraviolet absorption maxima in 0.035% hexane solution at 280, 270 (both sharp), and 254 mμ (indistinct), an additional yield (11 mg.) being obtained from the mother liquors.

The substance is unstable in air and must be kept in vacuum or in the atmosphere of carbon dioxide. It rapidly became yellow when it was dried at 100° in vacuum over phosphorus pentoxide. For analysis the substance was dried in vacuum at room temperature over calcium chloride.

Found:	(1)	C, 82.69; H, 10.96
	(2)	C, 81.49; H, 10.85
Calculated for $C_{28}H_{42}O$:		C, 85.21; H, 10.74
$C_{28}H_{42}O+\frac{1}{2}H_2O$:		C, 83.30; H, 10.75
$C_{28}H_{42}O+H_2O$:		C, 81.47; H, 10.75
$C_{28}H_{44}O$:		C, 84.76; H, 11.19
$C_{28}H_{44}O+\frac{1}{2}H_2O$:		C, 82.87; H, 11.19
$C_{28}H_{44}O+H_2O$:		C, 81.08; H, 11.19%

Reactions of Iso-dehydroergosterol. In the Liebermann-Burchard test iso-dehydroergosterol gives red, violet, and deep blue colours, while in the Rosenheim test instantly pink, light violet after five minutes, then blue, and finally dark violet colours.

When iso-dehydroergosterol (3 mg.) dissolved in a few drops of 95% alcohol was mixed with a 1% alcoholic solution of digitonin (10 mg.), precipitation of the digitonide took place instantly and was completed in a few minutes.

The Synthetic Preparation of Iso-neoergosterol from Neoergosterol and Iso-dehydroergosterol. When equal quantities (12 mg. each) of neoergosterol (m.p. 153.5–154.5°, corr.) and iso-dehydroergosterol (m.p. 127–129.5°, corr.) were dissolved together in a small amount of acetone with warming and the solution was cooled, there occurred separation of fine colourless needles (19 mg.) melting at 138.5–140° (corr.). Recrystallization gave iso-neoergosterol in colourless fine needles melting at 138–139° (corr.) alone and in admixture with the specimen obtained from the pyrolysis of ergopinacone. The synthetic product showed a specific rotation $[\alpha]_D^{11°} = -66.1°$ (6.8 mg. in 1 c.c. chloroform solution, $l = 1$ dm., $\alpha_D^{11°} = -0.45°$).

A depression of the melting point was observed when the synthetic iso-neoergosterol was melted with a very small quantity of either neoergosterol (mixed melting point 135–138°, corr.) or iso-dehydroergosterol (mixed melting point 128.5–134.5°, corr.).

The author's cordial thanks are due to Prof. Y. Urushibara for his kind guidance and encouragement. The author expresses his gratitude also to Mr. Y. Yamaguchi and to Oji Seishi Co. for generous help.

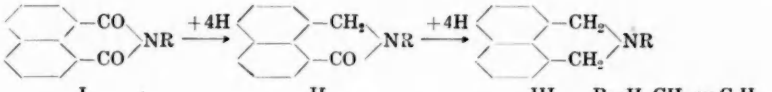
Chemical Institute, Faculty of Science,
Imperial University of Tokyo.

Electrolytic Reduction of Naphthalimide and its Derivatives.

By Buhei SAKURAI.

(Received April 10, 1939.)

So far as the author is aware, no one has yet succeeded in reducing naphthalic acid imides by purely chemical means. Electrolytically, however, both carbonyls in the imides may successfully be reduced as in the case of other dibasic acid imides, when zinc amalgam[1] is used as the cathode.



I *N*-Alkyl-naphthalimide

II *N*-Alkyl-naphthalimidine

III *N*-Alkyl-hydrobenzoisoquinoline

In the reduction experiments E. Späth[2] and his collaborator used lead cathode in a 50% sulphuric acid solution passing the current of 45 amp. per 100 sq. cm., and reported to have obtained 15% hydrobenzoisoquinoline as the final reduction product. By working under exactly the same condition the author could procure no reduction product, and even with the cathode of zinc amalgam the result was not much improved.

In order to find out better conditions for electrolytic reduction several experiments were performed by controlling concentration of sulphuric acid, current density, temperature of electrolyte, etc., but all were fruitless. Influence of alcohol added to the electrolyte with the object of increasing the solubility of the imide was found out to bring no better results.

In the case of its derivatives such as *N*-methyl-naphthalimide and *N*-ethyl-naphthalimide reduction took place with much ease. They were reduced with fairly good yield in sulphuric acid solution with cathode and produced *N*-methyl-naphthalimidine and *N*-ethyl-naphthalimidine respectively. The reduction stopped here without going further than this stage. For their complete reduction cathode of much stronger reducing power, such as zinc amalgam was required.

Experimental.

The materials used in the experiment were prepared in the following way.

Naphthalic acid was first prepared from acenaphthene by oxidizing it with powdered potassium bichromate in a warm glacial acetic acid solution, and naphthalic acid anhydride thus obtained (yellow powder, melting at 270°) was heated in a retort to which a current of ammonia was constantly passed and then cooled till it became

(1) B. Sakurai, this Bulletin, **7** (1932), 155; **10** (1935), 311.
(2) E. Späth and F. Brausch, *Univ. Wien, Monatschr.*, **50** (1928), 349.

a lump. The lump was taken out and crushed into powder and recrystallized from alcohol. Naphthalimide was thus prepared as reddish-brown powder, melting at 300°.

Methyl-naphthalimide was prepared by mixing naphthalic acid anhydride and methylamine in equivalent amount and recrystallized from alcohol after it was gradually heated on the water bath (yellow brown needle-like crystals, melting at 205°). Ethyl-naphthalimide (yellow needle-like crystals, m.p. 148°) was prepared in the same manner using ethylamine instead of methylamine.

I. **Naphthalimide** (I, R=H). Naphthalimide and its derivatives are insoluble in sulphuric acid solution. When one or both of two carbonyl groups are reduced into methylene groups, the basicity of molecules increases considerably, and in consequence they become soluble in the acidic electrolyte forming soluble salt. Thus the progress of reduction is clearly indicated by gradual disappearance of the imides suspended in the electrolyte. The experiments were conducted with lead cathode by controlling concentration of sulphuric acid (30–90%), temperature (26–60°), and current density (5–12 amp. per 100 sq. cm.), in various manners, but in no case the material was seen to dissolve in electrolyte. As the reduction was perceived to take place with zinc amalgam cathode, the best conditions of electrolysis were sought as follows. Cathode: zinc amalgam, 16 sq. cm. of area. Catholyte: mixture of 50 c.c. of 90% H_2SO_4 and 50 c.c. of alcohol and 1 g. of naphthalimide was added to it. Anode: cylindrical lead plate. Anolyte: 90% H_2SO_4. Current density: 105.3 amp. per 100 sq. cm. Time of electrolysis: 10 hours. Current quantity: 1234.9 F. per mol. Temperature: 30°.

Into the anolyte contained in a cylindrical biscuit vessel a cell containing catholyte was dipped, and a spiral lead tube was inserted into the cathode chamber. Cold water was passed through the tube to cool catholyte from inside, while the electrolyte bath itself was cooled all the time from outside with cold water. After 10 hours' electrolysis the catholyte still containing a considerable amount of undissolved substance was taken out and heated on the water bath to drive off alcohol. It was then diluted with about three times as much water and filtered. 0.69 g. of unreduced substance was obtained. The acidic solution was then shaken with ether several times in order to extract original imide remaining unreduced. About 0.14 g. of another unreduced substance was obtained. The aqueous solution was then made alkaline with caustic soda and treated with ether yielding thereby a small quantity of a brownish substance.

The platinum double chloride of this substance melted at 198° with decomposition. (Found: Pt, 26.04. Calculated for $[C_{12}H_{11}N]_2H_2PtCl_6$: Pt, 26.10%). The yield of the dihydrobenzoisoquinoline was found to be 8%.

II. ***N*-methyl-naphthalimide** (I, R=CH_3). (1) *Reduction with lead cathode.* With the view of obtaining *N*-methyl-naphthalimidine, reduction was conducted in sulphuric acid solution with lead cathode under the following conditions. Cathode: cylindrical lead plate, 100 sq. cm. of area. Catholyte: 1 g. of imide was suspended in 100 c.c. of 50% H_2SO_4. Anode: cylindrical lead plate. Anolyte: 50% H_2SO_4. Current density: 5 amp. per 100 sq. cm. Current quantity: 393.6 F. per mol. Temperature: 40°.

The electrolysis was carried out by cooling the electrolytic bath from outside with cold water, keeping the catholyte always in a vigorous agitation. The imide appeared to have dissolved fairly well. But 10 hours' electrolysis seemed to have been still insufficient as 0.57 g. of the original imide was detected remaining unchanged. This was filtered, and the filtrate was extracted with ether, when 0.059 g. of some other unreduced substance was obtained. The solution was made alkaline with caustic soda solution and again extracted with ether. About 0.3 g. of brown oily substance with a peculiar smell was obtained. This was easily soluble in hydrochloric acid solution and formed white needle-like crystals. Its platinum double chloride formed orange-coloured crystals melting at 172° with decomposition. (Found: Pt, 24.27. Calculated for $[C_{13}H_{11}NO]_2H_2PtCl_6$: Pt, 24.28%). The substance is thus regarded undoubtedly as *N*-methyl-naphthalimidine.

In the electrolysis with lead cathode reduction seems not to proceed further than the first stage. As the concentration of sulphuric acid has a close relation to reduction rate, a series of experiments were carried out by varying the concentration of sulphuric acid, results of which are summarised in Table 1.

From the table it is seen that the amount of unreduced substance decreases, as the concentration of sulphuric acid increases, making the reduction rate more than 30% in 50% solution of sulphuric acid. If, however, the concentration of sulphuric acid exceeds 50%, the yield of the reduced substance shows no remarkable increase despite the considerable decrease of the undissolved substance. Perhaps this is due to the fact that the imide partly polymerises into an unreducible substance on account of the high concentration of sulphuric acid. A resinous substance which may be regarded as such a polymer was always obtained, when electrolysis was conducted with the catholyte containing more than 70% of sulphuric acid.

Table 1.

Conc. of H_2SO_4 (%)	Undissolved material (%)	Ether extract from acidic medium (%)	*N*-methyl-naphthal-imidine (%)
20	91	—	4.5
30	75	—	14
40	67	—	23
50	57	5	32
60	55	9	30
70	30	21	36
80	20	35	33

As *N*-methyl-naphthalimide is slightly soluble in alcohol, though it is insoluble in sulphuric acid, electrolysis was carried out with a solution to which an equal volume of alcohol was added. The results are shown in Table 2.

As is seen from the table, the solution containing 40% of sulphuric acid gives the best results. When sulphuric acid becomes more concentrated the reduction rate falls rapidly, which shows that the effect of alcohol is rather harmful. Probably alcohol acts to enhance the resinification of the material, which is responsible for the rapid increase of ether extract from acidic medium containing more than 70% sulphuric acid.

Table 2.

Conc. of H_2SO_4 (%)	Undissolved material (%)	Ether extract from acidic medium (%)	*N*-methyl-naphthal-imidine (%)
40	25	10	49
50	30	11	27
60	42	15	19
70	10	60	20
80	13	51	18
90	11	59	22

(2) *Reduction with zinc amalgam cathode.* For the purpose of obtaining the complete reduction product of *N*-methyl-naphthalimide, i.e. *N*-methyl-hydrobenzoisoquinoline, zinc amalgam was taken as the cathode under the following conditions. Cathode: zinc amalgam 16 sq. cm. Catholyte: 100 c.c. of 50% H_2SO_4 in which 1 g. of imide was suspended. Anode: cylindrical lead plate. Anolyte: 50% sulphuric acid. Current density: 75 amp. per 100 sq. cm. Time of electrolysis: 6 hours. Current quantity: 566.9 F. per mol. Temperature: 34°.

Electrolysis was carried out by cooling the electrolytic bath, from outside with cold water and from inside by passing cold water through a spiral lead tube inserted to the catholyte, which was always kept vigorously stirring. Though the imide did not readily dissolve in the electrolyte, yet its amount was observed to diminish by degrees. At the beginning of electrolysis the experiment was much disturbed by hydrogen bubbles evolved at cathode, but it was soon found that this was easily prevented by dropping a small quantity of alcohol into it. After 6 hours' electrolysis the catholyte was diluted with about double volume of water and then filtered, when about 0.55 g. of insoluble substance was isolated. The filtrate was then treated with ether, and from the ether extract a small amount of light yellow fine needle-like crystals was obtained. This substance melted at 205° and was found to be unreduced material.

Now the remaining solution was made alkaline with caustic sode solution and then subjected to steam distillation. After making the distillate acidic with dilute hydrochloric acid it was evaporated to dryness. 0.2 g. of a substance in the form of white powder was left as the residue. That this substance was nothing but the hydrochloride of desired *N*-methyl-hydrobenzoisoquinoline was proved by analysing its platinum double salt obtained as beautiful orange-coloured crystals melting at 212° under decomposition. (Found: Pt, 25.15. Calculated for $[C_{13}H_{13}N]_2H_2PtCl_6$: Pt, 25.15%).

The solution, from which *N*-methyl-hydrobenzoisoquinoline was extracted with ether, was distilled with steam to drive off the base still remaining, and again treated with ether. After evaporating ether from the ether extract the aqueous solution was acidified with hydrochloric acid and evaporated to dryness. 0.05 g. of white powder was yielded. The platinum double chloride of this substance, melting at 170°, was identified as the double salt of *N*-methyl-naphthalimidine formed by electrolysis at lead cathode.

With the view of investigating the relation between the concentration of sulphuric acid and the reduction rate, a series of experiments was carried out by using as catholyte a mixture of equal volume of alcohol and sulphuric acid solution of various concentrations. Each electrolysis was continued for ten hours and the results are as shown in Table 3.

Table 3.

Conc. of H_2SO_4 (%)	Undissolved material (%)	Ether extract from acidic medium (%)	*N*-methyl-hydro-benzo-iso-quinoline (%)	*N*-methyl-naphthal-imidine (%)
50	31	20	21	5.0
60	17	20	26	4.5
70	13	21	29	5.9
80	20	23	27	4.4
90	14	29	38	4.5

As is seen from the above table, the greater was the concentration of acid the less was the undissolved material, and at the same time the more the yield of *N*-methyl-hydrobenzoisoquinoline. The concentration of sulphuric acid seems to exert no influence upon the yield of *N*-methyl-naphthalimidine, which remains almost constant. When the concentration of sulphuric acid becomes more than 70%, the quantity of the ether extract from acidic medium is observed to increase gradually. This is probably due to polymerization of the material, as was stated above.

III. **N-ethyl-naphthalimide** (I, R=C_2H_5). (1) *Reduction with lead cathode.* In order to get the reduction product of the first stage, i.e. *N*-ethyl-naphthalimidine, electrolysis was tried with lead cathode under the following conditions. Cathode: cylindrical lead plate, 100 sq. cm. of area. Catholyte: 100 c.c. of 60% sulphuric acid solution in which 1 g. of imide was added. Anode: cylindrical lead. Anolyte: 50% sulphuric acid. Current density: 6.5 amp. per 100 sq. cm. Time of electrolysis: 10 hours. Current quantity: 546 F. per mol. Temperature: 35°.

Electrolysis was conducted just in the same manner as in the case of the methyl derivative. When electrolysis stopped, a great quantity of insoluble substance still remained suspended in the solution. This was filtered off and 0.68 g. of unreduced substance was obtained. The filtrate was then treated with ether and from the ether extract 0.10 g. of unreduced substance was further produced. The electrolyte was then made alkaline with caustic soda and treated with ether, when a small amount of a yellowish oily substance soluble in hydrochloric acid was obtained. Its platinum double chloride was formed as yellow-brown crystals, melting at 165° with decomposition. (Found: Pt, 23.44. Calculated for $[C_{14}H_{15}NO]_2H_2PtCl_6$: Pt, 23.46%).

This reduction product was identified to be *N*-ethyl-naphthalimidine. The reduction rate was calculated to be 15.4%.

The results of investigation carried out to determine the relation between the concentration of sulphuric acid and the reduction rate are summarized in Table 4.

Table 4.

Conc. of H_2SO_4 (%)	Undissolved material (%)	Ether extract from acidic medium (%)	*N*-ethyl-naphthalimidine (%)
40	82	8	4.5
50	78	10	6.3
60	68	10	15.4
70	75	8	9.1
80	47	30	9.1
90	45	35	10.9

As 80–90% sulphuric acid solution caused foaming of catholyte, which made electrolysis very troublesome, a little amount of alcohol was added to catholyte. In consequence, insoluble substance remarkably decreased, while the part extracted with ether from acid solution increased. The concentration of 60% was found to be most favourable for reduction.

The results of the electrolysis showing the relation of the concentration of sulphuric acid to the reduction rate, when worked with catholyte containing an equal volume of alcohol, are shown in Table 5.

Table 5.

Conc. of H_2SO_4 (%)	Undissolved material (%)	Ether extract from acidic medium (%)	*N*-ethyl-naphthalimidine (%)
40	92	3	1
50	70	19	2
60	72	15	3
70	68	15	2
80	70	16	2
90	71	18	2

(2) *Reduction with zinc amalgam cathode.* With the view of obtaining the complete reduction product electrolysis was carried out with zinc amalgam cathode under the same conditions as were used in reduction of the corresponding methyl derivative. They were as follows. Cathode: zinc amalgam, 16 sq. cm. of area. Catholyte: mixture of 50 c.c. of 50% H_2SO_4 and 50 c.c. of alcohol in which 1 g. of the imide was introduced. Anode: cylindrical lead plate. Anolyte: 50% H_2SO_4. Current density: 75 amp. per 100 sq. cm. Time of electrolysis: 10 hours. Current quantity: 103.7 F. per mol. Temperature: 26°.

The material dissolved readily in the course of electrolysis and reduction seemed to take place far more smoothly than with lead cathode. But its dissolution was not completed even at the end of electrolysis. The catholyte was heated on the water bath to drive off alcohol and then it was diluted with double volume of water. 0.3 g. of undissolved material thus precipitated was filtered, and the filtrate was treated with ether, when 0.3 g. of unreduced substance was extracted. The filtrate was now made alkaline with caustic soda solution, and subjected to steam distillation, collecting the distillate in dilute hydrochloric acid solution as long as it continued to react alkaline. The hydrochloric acid solution was then evaporated to dryness on the water bath, when 0.21 g. of white powder was left as the residue. The platinum double chloride prepared from the residue was beautiful orange-coloured crystals melting at 197° with decomposition. (Found: Pt, 24.29. Calculated for $[C_{14}H_{12}N]_2H_2PtCl_6$: Pt, 24.28%).

On treating the remaining solution after steam distillation with ether a small amount of oily substance was extracted. Its platinum double chloride melted at 165° and was identified as N-ethyl-naphthalimidine. The yield was 5.4%. In order to obtain the relation of the reduction rate to the concentration of acid, a series of

electrolyses were carried out by varying the concentration of acid. The results are summarized in Table 6.

Table 6.

Conc. of H_2SO_4 (%)	Undissolved material (%)	Ether extract from acidic medium (%)	*N*-ethyl-hydro-benzo-iso-quinoline (%)	*N*-ethyl-naphthal-imidine (%)
30	47	19	24	5.1
40	37	25	18	2.2
50	30	30	21	5.4
60	25	31	14	5.4
70	23	31	15	5.4
80	21	33	17	5.4
90	—	30	44	6.1

As is seen from the table, the greater was the concentration of the acid, the more soluble became the material, and at 90% it completely dissolved, but the ether extract did not increase in the same proportion. The yield of the complete reduction product remarkably increased at 90%. The yield of *N*-ethyl-naphthalimidine, independent of the concentration of acid, remained nearly constant, as in the case of the corresponding methyl derivative.

The author expresses his sincere thanks to Dr. Motooki Matsui, Professor emeritus of the Kyoto Imperial University, for his cordial suggestions.

The Osaka Women's College,
Sumiyoshi, Osaka.

Studies on Rhythmic Precipitates.

By Toshizo ISEMURA.

(Received November 24, 1938.)

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I. Introduction.

In 1896 Liesegang discovered that when silver nitrate solution was allowed to diffuse into a gel impregnated with a small quantity of potassium dichromate, the deposition of the silver chromate in the gel was not continuous but marked by gaps or empty spaces at regular intervals.[1] Percieving the importance of the phenomenon he studied this phenomenon systematically[2] which was then followed by many other investigators.[3] As the result of their investigations, it was observed that not only silver chromate but also some other scarsely soluble substances form rhythmic precipitates. It was ascertained, that in many precipitation reactions rhythmic bands are obtained, when two reactive substances are brought in contact with each other, by diffusing one of the substances into a solution of the other in a gel. Since then it attracted the interest of the investigators in the question: what mechanism the phenomenon is produced by? At first, Wilh. Ostwald proposed a theory to explain this phenomenon, which is known to-day as the "super-saturation theory".[4] Ever since many other theories were presented by different authors,[5] yet this phenomenon cannot be fully explained by these hitherto proposed theories.

The present author studied the rhythmic precipitates from various standpoints, the description of which is given in the following pages. A number of new examples were obtained in the course of study, and it was made clear that in several examples the rhythmic precipitates, which are considered hitherto as Liesegang phenomenon, are produced by the periodic changes of external conditions such as light or temperature. It has been studied on the effect of the varieties of gel, the electrolytes, the hydrogen ion concentration, the presence of impurities and other substances, the ageing of gel, the light and the temperature on the formation of rhythmic precipitates. It was also studied a general regularity with regard to the intervals of the bands.

II. Various Influences on the Formation of Rhythmic Precipitates.

The Influence of the Nature of Gel. Rhythmic precipitates are formed not only in a gel but also in places such as capillary tubes or narrow aperture between two glass plates where no gel is present. The formation of rhythmic precipitates in a gel will be described first.

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(1) Liesegang, *Naturw. Wochschr.*, **11** (1896), 353; *Photographisches Archiv*, (1896), 221.

(2) Liesegang, *Kolloid-Z.*, **2** (1998), 70; *Z. physik. Chem.*, **88** (1914), 1; "Chem. Reaktionen in Gallerten" Düsseldorf, (1898); "Geologische Diffusionen", Dresden, (1913).

(3) See Hedges, "Liesegang rings"; S. Veil, "Les Phénomènes Périodiques de la Chimie" Paris, (1934).

(4) *Z. physik. Chem.*, **23** (1897), 365; "Lehrbuch der Allgemeinen Chemie" II, 2, 777, Leipzig, (1911).

(5) Bradford, *Kolloid-Z.*, **30** (1922), 364; Chatterji and Dhar, *Kolloid-Z.*, **31** (1922), 15; *ibid.*, **37** (1925), 2, 89; Wo. Ostwald, *Kolloid-Z.*, **36** (Zsigmondy-Festschrift) (1925), 380; Holmes, *J. Am. Chem. Soc.*, **40** (1918), 1187; Fischer and Mclaughlin, *Kolloid-Z.*, **30** (1922), 13; Traube and Takehara, *Kolloid-Z.*, **35** (1924), 245; Michaleff, Nikiforoff and Schemjakin, *Kolloid-Z.*, **66** (1934), 197; Christiansen and Wulff, *Z. physik. Chem.*, B, **26** (1934), 187.

As Liesegang[1] had first found, the rhythmic precipitation of silver chromate is well developed in a gelatine jelly, but generally not in an agar-agar or in a silicic acid gel. This is known as a specific influence of a gel on the formation of rhythmic bands. Moreover, even though a gel is made of gelatine, the same results may not be obtained with various gelatines from different manufacturers.

The present author carried out three series of experiments. In the first series, five kinds of gelatines were used, two of which, being the products of our country, were purchased from Takeda Pure Chemicals & Co. and were denoted by A and B, while the others were also purchased from Takeda but manufactured by Coignet Père et Fils & Co. in Belgium and were denoted by A, D, and No. 1. In the gels which were made from these gelatines under entirely the same conditions, it was tried to make rhythmic precipitate of silver chromate. 3% gelatine solutions containing 0.1% potassium dichromate were made and introduced into test tubes (diameter about 10 mm.) to the height of 7 cm. After the gel set firmly, 5% silver nitrate solution was poured on it. The test tubes were kept in a dark room.

In Japanese gelatine A no distinct rhythmic bands were formed but at the transition zone from the fine brick-red precipitates to the relatively coarse dark violet precipitates, some faint bands were seen. In Japanese gelatine B, 8～9 distinct bands were found under a continuous zone of brick-red precipitate, beneath which a layer was formed of uniformly scattered dark violet precipitate, and in the lower part of the test tube there were 6 violet bands which consisted of relatively coarse precipitate. On the other hand, in all other three gelatines, which were made in Belgium, the typical rhythmic precipitate of brick-red silver chromate was well developed. In gelatine A of Coignet, 25 bands were formed. In this case, the intervals between two succeeding bands were the shortest among the three examples. In gelatine No. 1. of Coignet, 21 bands were formed. In gelatine D of Coignet, 20 bands were formed and the intervals between them were the longest among these three.

The second series of experiment were conducted in the same manner, with seven samples of photographic gelatines, A, B, and C for the manufacture of positive cinematographic film and A, B, C and D for negative film. These photographic gelatines were placed at the author's disposal by the kindness of Fuji Photo Film Co. Ltd. The conditions were entirely the same as those of the first series. The results were as follows. In gelatine A for positive film, 15 bands were recognised, though seven of which were very faint. In gelatine B for positive film, 26 bands were formed, the lower the position of the band formed in the gel was, the smaller the diameter of the disc of band. The density of the band formation was large. In gelatine C for positive film, 26 distinct bands were formed, and in this case also, the lower the position of the band the smaller the diameter of the disc. In gelatin A for negative film, 12 bands were formed, though all were faint, four of them were especially very faint. In gelatine B for negative film, 30 bands were formed. The band was too dense and a part of the banded precipitate was blurred. The banding was the same type with gelatine B for positive film. In gelatine C for negative film 15 bands were formed, seven of

which being very faint. The appearance of this rhythmic precipitate was similar to that in gelatine A for positive film. In gelatine D for negative film, 17 bands were formed, the typical rhythmic precipitate being well developed.

In the third series, an attempt was made to make bands of magnesium hydroxide in these photographic gelatines. In this case, the specific influence of gelatines was more or less indistinct. In gelatine A for positive film, 2 bands and a band of saturn structure were formed. In gelatine B for positive film, 2 bands and a ring were formed. In gelatine C for positive film, 2 bands and a ring were formed. In gelatine A for negative film also, 2 bands and a ring were formed, but in this case the intervals between the bands were somewhat larger than the cases of gelatine B and C for positive film. In gelatine B for negative film, 2 bands and a ring were formed, the intervals between them were the same as in the cases of gelatine B and C for positive film. In gelatine C for negative film, 2 bands and a band of saturn structure were formed and in gelatine D for negative film, 3 bands were formed. The differences of bands in the case of magnesium hydroxide caused by the varieties of gelatine were somewhat obscure but recognisable.

Thus the different gelatines give entirely diverse results. It seems that these effects may be chiefly referred to the hydrogen ion concentration of the gel and to the impurities contained in gelatine. Liesegang[6] concluded that the specific influences of gelatines on the formation of rhythmic precipitates are referred to the content of gelatose, a hydrolytic product of gelatine.

By the author's experiment, however, it was recognised that the influence of the difference of gelatose content is not so large, for the banding was scarcely influenced by the addition of a small quantity of gelatose to the gel. Accordingly, the influence of the species of gelatines is not referred only to the gelatose content.

Certain rhythmic precipitate is formed in gelatine, in agar-agar, or in silicic acid gel, irrespective of the species of the medium, or even in the complete absence of gel. For example, the rhythmic precipitate of calcium phosphate is the case. It is well known that calcium phosphate forms rhythmic precipitate in gelatine, in agar-agar or in the complete absence of gel. The author could obtain the rhythmic bands of this substance also in silicic acid gel.[7]

On the other hand, it is well known that silver chromate gives a typical rhythmic precipitate in gelatine jelly but not in agar-agar or in silicic acid gel. Bradford[8] obtained silver chromate bands in an agar-agar gel which contained somewhat large quantity of potassium citrate with potassium dichromate. Hatschek[9] had succeeded in obtaining the bands of silver chromate in a silicic acid gel, which was prepared by the unusual method, based on the fact that silicic acid is gelatinised on mixing

(6) Liesegang, *Kolloid-Z.*, **2** (1907), 70.
(7) Isemura, this Bulletin, **13** (1938), 493.
(8) Bradford, "Alexander's Colloid Chemistry, Theoretical and Applied" Vol. I, 790, New York (1926).
(9) Hatschek, *Kolloid-Z.*, **38** (1926), 151.

a solution of sodium silicate with somewhat large quantity of a solution of potassium dichromate.

As reported in a previous communication,[10] the present author had also succeeded in obtaining more distinct rhythmic bands of silver chromate in a silicic acid gel which was prepared by the usual procedure. A sol was prepared by mixing a solution of sodium silicate with some acids and then potassium dichromate was added. After the gel set firmly, a strong silver nitrate solution was put on it and let diffuse into the gel. Silver chromate bands in a silicic acid gel were thus obtained. In this case, hydrogen ion concentration of the gel plays an important rôle, and the range of *p*H where the rhythmic precipitates are made, is very narrow. So, it was believed by many investigators, that silver chromate cannot be obtained in bands in silicic acid gel and they insisted upon the non-formation of bands as being the specific effect of gel. The rhythmic precipitates of the same substance are produced in various jellies by modifying the conditions in certain degree.

Lead chromate does not form rhythmic bands in an ordinary silicic acid gel, but forms bands in the presence of some glucose in the gel.[11] Lead iodide in a silicic acid gel does not form rhythmic precipitate in an ordinary condition and fern-like fronds grow down into the gel, mixed with many hexagonal plates. But it was found in rare cases that the rhythmic precipitate of this substance occurred accidentally. When the crystal became relatively small, the rhythmic precipitate was generally formed. The increase of the concentration of inner and outer electrolytes is favourable for making the deposited crystals small. In order to make sure of the formation of the rhythmic precipitate of lead iodide a third substance has to be added, which makes the crystals of lead iodide very small. Citrate and tartrate fit for this purpose. The typical rhythmic bands of lead iodide in a silicic acid gel were obtained by the presence of a small quantity of citrate or tartrate.[12] These results will be described later in detail.

It seems from the above-mentioned results that the nature of gel has a great influence on the formation of periodic precipitate but rhythmic bands are produced in any gel when we modify the condition appropriately. Generally the precipitates formed in gelatine are especially small in size. The precipitates formed in silicic acid gel on the contrary, are often well-developed crystals, and the bands are often blurred by the growth of too large crystals which came in contact with each other.

The presence of a gel is favourable in many cases but not always necessary for the formation of bands. This was already shown by Dreaper[13] and others.[14] In their experiments rhythmic precipitation was observed in a capillary tube of in a narrow aperture between two glass plates and the formed rhythmic bands are always microscopic. We can recognise from these facts, that the gel has an important signifi-

(10) Isemura, this Bulletin, **13** (1938), 489.
(11) Isemura, *ibid*, **8** (1933), 11.
(12) Isemura, *J. Chem. Soc. Japan*, **58** (1937), 58.
(13) Dreaper, *Kolloid-Z.*, **14** (1914), 163.
(14) Wo. Ostwald, *Kolloid-Z.*, **40** (1926), 144; Notboom, *ibid.*, **32** (1923), 247; Morse, *J. Phys. Chem.*, **34** (1930) 1554; Ghosh, *J. Indian Chem. Soc.*, **7** (1930), 509.

cance to prevent the disturbances caused by heat convection or by mechanical shocks. If the reactions are undertaken in a viscous fluid and mechanical shock is prevented and the sudden change of temperature is avoided, then rhythmic bands may be produced in an ordinary test tube in the absence of jelly. When the density of the precipitate produced by such reaction in the viscous fluid is large, the precipitate settles down by gravity so that the bands blur.

In some colour reactions, however, bands are preserved for a long time. For example, the reaction which is known as Lunge's reaction for nitrate ion, gives often rhythmic bands when the system is kept from disturbances. A dilute potassium nitrate solution is gently run down the side of a test tube on a diphenylamine solution in concentrated sulphuric acid, and the tube is allowed to stand for several days. Blue rhythmic bands, are formed in sulphuric acid. Similar rhythmic colourings were observed in some other colour reactions. Reaction between an aqueous solution of egg albumin and a solution of α-naphthol or thymol in sulphuric acid, which is called Molisch's reaction for sugar in protein, gives violet or red-brown bands. The reaction of an aqueous solution of egg albumin with a solution of glyoxylic acid in sulphuric acid, that is known as the Hopkins and Cole's reaction for protein, gives blue violet rhythmic colouring in the entire absence of disturbance. Fig. 1 shows the rhythmic colouring of the reaction of protein with α-naphthol and thymol. The left photograph is obtained by the reaction of protein with thymol and the right by the reaction with α-naphthol. When we carefully protect the test tubes from shocks and sudden change of temperature, we can preserve these bands for a long period.

The Influence of Inner Electrolyte and its Concentration. The range of the concentration of inner and outer electrolytes for the formation of the Liesegang rings is rather narrow. Accordingly, it gives the general appearance that the formation of rhythmic precipitate is limited to some speciai substances. In the author's opinion, however, the formation of periodic precipitate is a general phenomenon.

The concentration of inner electrolyte has especially a profound influence on the formation of bands. The concentration of electrolyte beyond a certain limit is necessary for the formation of bands. The increase of the concentration of inner electrolyte beyond this limit makes the banding more dense. The distance from the top of the gel to the first separted band becomes large with the increase of the concentration of inner electrolyte. On the other hand, if the concentration exceeds certain upper limit, bands can no more be obtained.

The increase of the concentration of inner electrolyte hinders the diffusion of outer electrolyte into a gel, while the inner electrolyte diffuses in the opposite direction, so that there remains little reactant at the bottom of the test tube. Consequently, the distance between the last formed band and the top of the gel becomes short when the bands deposit closely each other. The relation between the density of bands and the change of concentration of inner electrolyte was shown in the previous communications.[15] Some of the results are given in the following tables.

(15) Isemura, *J. Chem. Soc. Japan*, **58** (1937), 301, 629.

Table 1.

Bands of Silver Carbonate.

Conc. of sodium carbonate (inner electrolyte) (%)	Number of bands
0.25	continuous precip.
0.23	continuous precip.
0.20	10
0.15	5
0.12	4
0.10	3
0.08	0
0.06	0

Gelatine 2.8%.
Outer electrolyte: silver nitrate 5%.
Temperature: 5°C.

Table 2.

Bands of Silver Carbonate.

Conc. of ammonium carbonate (inner electrolyte) (%)	Number of bands
2.3	13
1.4	15
0.9	12
0.6	9
0.5	8
0.4	7
0.3	5
0.2	6
0.1	3

Gelatine 2.8%.
Outer electrolyte: silver nitrate 5%.
Temperature 5°C.

Table 3. Bands of Silver Iodate.

Conc. of silver nitrate (inner electrolyte) (%)	Total number of bands	Number of bands *
0.17	20	15
0.13	22	14
0.09	22	13
0.07	22	12
0.04	10	3

Gelatine 2.8%. Outer electrolyte: potassium iodate 5%. Temperature: 5°C.

The asterisk denotes the number of bands formed from 10 to 40 mm. from the contact surface of the diffusing solution and gel. (The same in Tables 3, 5, 7, 12, 14, 16).

Table 4. Bands of Silver Arsenite.

Conc. of sodium arsenite (inner electrolyte) (%)	Total number of bands	Number of bands **
1.8	28	16
1.0	29	18
0.7	27	19
0.3	26	18
0.2	20	17
0.1	14	11

Gelatine 2.5%. Outer electrolyte: silver nitrate 5%. Temperature: 10°C.

** denotes the number of bands formed 30 to 60 mm apart from the contact surface of the gel and the diffusing electrolyte. (The same in Tables 4 8, 13, 17).

Table 5. Bands of Lead Iodate.

Conc. of potassium iodate (inner electrolyte) (%)	Number of bands*
2.0	23***
1.8	25
1.6	23
1.4	22
1.2	20
1.0	20
0.8	19
0.6	17
0.4	14
0.1	8

Gelatine 2%. Outer electrolyte: lead acetate 0.5 mol.
Temperature: 15°C.

*** A continuous precipitate was formed to a point of 12 mm. from the contact surface and the bands could not be counted in the part 10 to 12 mm. apart from the surface.

In these cases, the effects of concentration of inner electrolyte were investigated keeping other conditions in same. Experiments were conducted in test-tubes the inner diameter of which being 1.2 cm. and the length, 11 cm. These test tubes were filled with the gel to the height of 6.5 cm. Fig. 2 shows the effect of concentration of inner electrolyte in the case of silver carbonate bands. These photographs correspond to the third to seventh experiments shown in Table 1.

The influence of the concentration of inner electrolyte was studied subsequently with barium chromate, lead carbonate in gelatine, lead carbonate, cobalt sulphide, ferric ferrocyanide, cobalt phosphate, copper iodate, copper carbonate and bismuth chromate bandings in silicic acid gels. These experimental results will be described later in details.

The appearance of the rhythmic precipitate of a certain substance, produced by the action of the various salts as the inner electrolyte, differs profoundly according to the kind of salt. For instance, when we make silver carbonate bands in gelatin, we can use ammonium carbonate as well as sodium carbonate. But the appearance of the obtained rhythmic bands is quite different in these cases. In the case of ammonium carbonate the bands are obtained for relatively wide range of the concentration of inner electrolyte, namely $0.1 \sim 2.3\%$, while in the case of sodium carbonate the range of concentration is rather narrow. Moreover the bands of silver carbonate which were made by using sodium carbonate as the inner electrolyte looked like tablets and were separated from each other with considerable intervals. The bands which were made by using ammonium carbonate, grew relatively close as seen in Table 2 and each band was often incomplete and had the appearance of a net-work or an assemblance of fragments of crescent-shaped precipitate. It seems that the influence

of the varieties of inner electrolyte is referred to the effect of the soluble reaction products, such as sodium nitrate or ammonium nitrate, on the solubility and growth of the precipitate.

The Influence of Outer Electrolyte and its Concentration. On the formation of rhythmic precipitate it is necessary that the outer electrolyte diffuses into the gel. So the concentration of the outer electrolyte must be high. At least it must be hypertonic to that of the inner electrolyte. The effect of the concentration of the outer electrolyte on the formation of periodic bands is similar in many cases. The higher the concentration is, the larger the number of bands becomes. The larger the ratio of concentration of outer electrolyte to that of inner electrolyte becomes, the closer the intervals between the bands, generally become. So, if the conditions, excepting the concentration of the outer electrolyte are maintained constant, it is obvious that the higher the concentration is, the larger the number of the formed bands and the smaller the intervals between the bands become. The importance of the concentration as to whether bands are formed or not, is smaller in this case than in the case of inner electrolyte, that is the range of concentration that can form rhythmic bands is very wide. But too concentrated solution is often unfavourable for the rhythmic banding. If the concentration becomes too high, the bands stand too close together, so a part of precipitate appears only like a column of precipitate and has not a periodic structure. At the same time, if too concentrated solution of outer electrolyte was used, it often peptised the gel. For example, when silver chromate bands are made in gelatine, too concentrated silver nitrate solution peptises the gelatine at the contact surface of the gel with the solution. For these reasons, the concentration of outer electrolyte is somewhat restricted, but in general, the concentration of outer electrolyte for the rhythmic banding has a relatively small significance. The results of the experiments on the influence of the concentration of outer electrolyte, were also shown in the previous communication.[15] Some of the results are given in the following tables.

Table 6.

Bands of Silver Carbonate.

Conc. of silver nitrate (outer electrolyte) (%)	Number of bands
20	9
15	8
10	7
5	6

Gelatine 2.8%.
Inner electrolyte:
sodium carbonate 0.17%.
Temperature 5°C.

Table 7. Bands of Silver Iodate.

Conc. of potassium iodate (outer electrolyte (%)	Total number of bands	Number of bands*
Saturated solution	22	13
5.0	21	12
4.0	17	9
3.0	13	6
2.0	12	2

Gelatine 2.8%.
Inner electrolyte: silver nitrate 0.1%.
Temperature 5°C.

Table 8. Bands of Silver Arsenite.

Conc. of silver nitrate (outer electrolyte) (%)	Number of bands**
15	15
10	26
5	15

Gelatine 2.5%.
Inner electrolyte:
sodium arsenite 0.67%.
Temperature: 10°C.

When a 15% silver nitrate solution was added the formed continuous precipitate came down to a distance of 43 mm. from the surface of the gel. Therefore, the bands decreased in number, but in reality they stood close by in the highest degree.

Table 9. Bands of Lead Iodate.

Conc. of lead acetate (outer electrolyte) (mol.)	Number of bands*
1.00	22
0.75	21
0.50	20
0.25	18

Gelatine 2.0%.
Inner electrolyte:
potassium iodate 1.2%.
Temperature: 15°C.

Fig. 3 shows the change of the closeness with the concentration of outer electrolyte in the case of silver carbonate bands.

The influence of the concentration of outer electrolyte was subsequently studied with lead carbonate, copper iodate, and cobalt sulphide bandings in silicic acid gels. In the case of calcium phosphate bands in the silicic acid gel, some peculiar results were obtained. While the concentration of outer electrolyte is relatively low, the general rule—the higher the concentration is, the larger the number of bands formed becomes or the smaller the intervals between the bands become—holds in this case also. But if the concentration exceeds a certain limit, the influence is scarcely observed as shown in Table 10. The rhythmic precipitates which were obtained by the diffusion of calcium chloride, the concentration of which were beyond a certain limit, are entirely identical[16].

Table 10. Calcium phosphate in silicic acid gel.

Conc. of calcium chloride (outer electrolyte) (%)	Number of bands	
30	8	These three coincide and showed no difference.
25	8	
20	8	
15	8	The bands were close in proportion to the concentration of outer electrolyte.
10	8	
5	7	

Inner electrolyte: sodium phosphate 0.5%.

As described in the foregoing paragraphs, bands of different appearance are obtained under the same experimental conditions when the

(16) Isemura, this Bulletin, **13** (1938), 493.

species of the inner electrolyte are different. Similarly, different bands are obtained, when the species of outer electrolyte differs. This is proved in the cases, for example, of the formation of periodic precipitates of lead iodate in gelatine, where lead nitrate and lead acetate solutions of the same concentration are used as the outer electrolyte respectively. When lead nitrate is used, the bands are thinner and their number is larger and the intervals between them become shorter than the case of lead acetate. Fig. 4 shows such a case, the left being obtained by diffusion of lead nitrate and the right by lead acetate. The bands stood so close in the case of lead nitrate, that scarcely any strata were discriminated in the upper part of the figure. This fact is not to be referred to the difference of the diffusibility of lead nitrate and lead acetate. It must preferrably be referred to the influence of the solubility of the precipitate in the formed soluble salts such as potassium nitrate and potassium acetate. Because, the effects of the temperature or the concentration of gel, which affect considerably the diffusibility, give smaller difference of bandings than the effect of the outer electrolyte. Even when a half concentrated solution of lead nitrate to that of lead acetate is used still closer the bands are formed than those formed by the diffusion of the lead acetate solution.

Rhythmic precipitates of bismuth chromate in silicic acid gel, obtained by diffusing bismuth nitrate and bismuth chloride have quite different appearances. In this case, the acid which is used to prepare the gel has also some effects on the bands. So this case will be treated later again.

Contrary to the effects of the concentration of outer electrolyte previously described, there are a number of cases in which, when the concentration of outer electrolyte increases, the intervals between the bands increase and the bands become more distinct. This is the case of gold banding. Indeed, gold bands are not formed as a true "Liesegang phenomenon" but as a reflex of the rhythms of external conditions. This will be described in the later part.

According to Lincoln and Hillyer,[17] if the ratio of the concentrations of outer and inner electrolyte is constant, the same distribution of the layers of rhythmic precipitate is obtained, providing that the gel concentration and the temperature are constant. By the decrease of the concentration of inner electrolyte the formation of precipitate becomes slower, and on the other hand, by the decrease of that of outer electrolyte, it diffuses more slowly, so the influences of the decrease of the concentration of both inner and outer electrolyte become relatively small, for both affect oppositely. But it seems that both influences are not completely compensated by each other. The present author studied this fact by using the bands of silver chromate in gelatine and calcium phosphate in silicic acid gel. These rhythmic precipitates, however, did not obey the above rule. So, it seems that the fact pointed out by Lincoln and Hillyer has no generality.

Interchange of Inner and Outer Electrolytes. When a rhythmic precipitate obtained by the interaction of two substances in a gel, either

(17) Lincoln and Hillyer, *J. Phys. Chem.*, **38** (1934), 907.

of the two may well become an inner electrolyte or an outer electrolyte. In many experiments by various authors, in which silver chromate bands are made in gelatine, potassium dichromate is usually dissolved in gelatine as an inner electrolyte and silver nitrate is allowed to diffuse into the gel. But, inversely, by diffusion of potassium dichromate into the gelatine containing silver nitrate, we can also obtain the rhythmic precipitate of silver chromate.

Accordingly, the interchange of inner and outer electrolytes has no concern with the formation of rhythmic precipitate as a general rule.

It is often impossible to add salts of heavy metals to the silicic acid gel, for silicic acid is partially coagulated. On the other hand, when silver carbonate bands are formed in gelatine containing ammonium carbonate by the diffusion of silver nitrate, a rhythmic precipitate which often consists of crescent-shaped bands is obtained. When the bands are formed reversely in gelatine containing silver nitrate as an inner electrolyte, we shall meet an interesting fact. At first silver carbonate bands have formed, but with the progress of diffusion to the lower part of the gel, the upper bands successively re-dissolved by the formation of a more soluble double or complex salt with the excess of diffusing ammonium carbonate. Owing to the deposition of precipitate in gel, the gel is broken at these parts of deposition. Later, being separated, these parts do not cohere again. There remain rhythmic cracks.

When lead iodide bands in a silicic acid gel are formed by the diffusion of potassium iodide into a gel containing lead acetate, well-developed rhythmic bands are obtained, although a part of lead iodide re-dissolve, forming a soluble complex salt at the top of the gel. But inversely, if lead acetate diffuses into a gel containing potassium iodide, lead iodide is formed at first, but it is immediately converted into a white double salt with successively coming lead acetate. In this case the bands are not so distinct.

In some cases the rhythmic bands of quite different appearances are obtained by the interchange of the inner and outer electrolytes. This is the case with rhythmic bands of silver iodate in gelatine. When a gel containing potassium iodate was covered with silver nitrate solution a rhythmic precipitate is obtained as shown in Fig. 5, the bands of which consist of flocculent clusters of crystals. On the contrary, when a gel containing silver nitrate was covered with the potassium iodate solution the formed rhythmic precipitate is very peculiar in shape, showing a greatly different form from any rhythmic precipitates which the author had ever seen. Fig. 6 shows this rhythmic precipitate. In this case, the structure is rather complicated, thus, band consisting of scattered coarse crystals, thin band consisting of very small crystals and relatively thick band consisting of coarse crystals and empty interspace were repeatedly observed.

The Influence of the Concentration of Gel. The concentration of gel has a remarkable influence on rhythmic precipitate. In many cases, if the concentrations of inner and outer electrolyte are kept constant, the number of formed bands decreases and the intervals between them increase with the increase of gel concentration. The distance from the

top of the gel to the last formed band also decreases, in general, with the concentration of the gel. The influence of gel concentration had been investigated on the rhythmic precipitates of silver carbonate, silver iodate, silver arsenite and lead iodate in gelatine gels. The results are shown in the following tables (Table 11–15).

Table 11.
Bands of Silver Carbonate.

Conc. of gelatine (%)	Number of bands
5.0	2
4.0	4
3.0	5
2.0	9

Inner electrolyte: sodium carbonate 0.17%.
Outer electrolyte: silver nitrate 5%.
Temperature: 5°C.

Table 12.
Bands of Silver Iodate.

Conc. of gelatine (%)	Total number of bands	Number of bands*
5.0	21	12
4.0	23	13
3.0	25	12
2.8	25	13
1.5	25	14

Inner electrolyte: silver nitrate 0.13%.
Outer electrolyte: potassium iodate 5%.
Temperature: 5°C.

Table 13. Bands of Silver Arsenite.

Conc. of gelatine (%)	Number of bands**
4.4	16
3.5	17
3.1	18
2.7	19
2.3	21

Inner electrolyte: sodium arsenite 0.67%.
Outer electrolyte: silver nitrate 5%.
Temperature: 10°C.

Table 14. Bands of Lead Iodate.

Conc. of gelatine (%)	Number of bands
6.0	16
4.8	18
3.0	20
2.0	23

Inner electrolyte: potassium iodate 1.6%.
Outer electrolyte: lead acetate 0.5 mol.
Temperature: 15°C.

Fig. 7 shows the effect of the concentration of gel in the case of silver carbonate bands in gelatine. The intervals between bands increase and the number of formed bands decreases with the concentration of gel. The influence of gel concentration was first investigated quantitatively by Popp[18] with rhythmic precipitate of magnesium hydroxide in gelatine. According to her experiment, the band itself and the intervals between bands increased with gel concentration, but the number of bands formed was unchanged. In a concentrated gel, the diffusion proceeds slowly and the gel acts to prevent the separation of precipitates. The above results seemed to show that the increase of gel concentration forced to decrease the diffusion velocity and to increase the action which prevents considerably the separation of precipitates.

(18) K. Popp, *Kolloid-Z.*, **36** (1925), 208.

There is an exceptional rhythmic precipitate that gives a reverse result to the above mentioned general rule. This is the case of silver chromate in gelatine. The results are shown in Table 15. In this case the number of bands increases and the intervals between bands decrease by the increase of gel concentration.

Table 15.

Bands of Silver Chromate.

Conc. of gelatine (%)	Number of bands
10.0	35
7.5	31
5.0	27
2.5	19

Inner electrolyte: potassium dichromate 0.13%.
Outer electrolyte: silver nitrate 30%.
Room temperature.

Indeed, there is a significance in the existence of gel for the prevension of the disturbance caused by convection and removing unfavourable effects caused by shocks. Rhythmic precipitate is generally obtainable either in dilute or concentrated gel. For the quickness of diffusion of outer electrolyte it is convenient to use a dilute gel which has the "form-stability" beyond a certain limit. In some special cases, however, it is better to use the concentrated gel, for it favours the accumulation of the precipitate. One of the example of this case is the gold banding in silicic acid gel. Gold bands are well developed in the gel which is prepared by mixing equal volumes of a 1.16 density water glass solution and a 3 N solution of sulphuric acid, but only faint bands are obtained in the gel prepared by mixing a solution of water glass ($d = 1.06$) and a 0.5 N sulphuric acid.

The Influence of Light. Experiments have been done on the rhythmic precipitates of various examples in the light and dark place, and it has been known that, in general, the rhythmic bands appear in light as well as in dark. But in one of the previous communication,[19] the author has reported that the light has a profound influence on certain rhythmic precipitate such as that of silver chromate in gelatine jelly. Light has an effect only on the photo-sensitive systems such as chromate-gelatine and an essential significance on the diurnally formed system.

Küster[20] stated that no band of silver chromate was obtained in the dark, while Davies[21] obtained good bands. Blair[22] reported that the bands formed in complete darkness show irregularity. The experiment carried out by the present author are as follows. Three samples of gelatine solutions were prepared, the first sample was made in complete darkness while the second and the third in an ordinary room. The first and the second were set in the dark place and the third, in an ordinary room. Three days later, silver nitrate solution was poured on these gels. After standing the former two in the dark and the latter in the light for a week, rhythmic precipitates of silver chromate were recognised in

(19) Isemura, this Bulletin, **8** (1933), 108.
(20) Küster, *Kolloid-Z.*, **13** (1913), 192.
(21) Davies, *J. Am. Chem. Soc.*, **44** (1922), 2698.
(22) S. Blair, *Phil. Mag.*, **49** (1925), 90.

all three test tubes and no irregularity was noticed. From this fact it has been ascertained that the formation of bands is not affected by the darkness.

According to Blair the bands become irregular when the gel has been irradiated with visible light. But Cluzet and Kofmann[23] stated that the formation of rhythmic precipitates was unaffected by visible light. The author found that the radiation of visible ray has an important effect on the formation of bands though the bands do not become irregular even by the strong irradiation of direct sun light. The experiment was done as follows: 2.5% gelatine gel containing potassium dichromate (0.1%) as an inner electrolyte was allowed to set in test tubes and they were kept in a dark place. After the gel set firmly, it was covered with 15% silver nitrate solution. Then each of the test tubes was exposed to direct sun light for different interval of time. The light was filtered through the layer of water to avoid the effect of heat ray. In this case, the number of the formed bands increases in proportion to the time of exposure. But when a certain time interval was exceeded, the bands formed too close to each other and the whole appeared as a dark brown column. Analogous results were obtained by the influence of diffused light.

We can conclude from these results, that the visible light caused to increase the number of bands and to decrease the distance between bands. It seems that these changes which are caused by the exposure to light, are due to the transformation of gel structure and to the interaction of gelatine and potassium dichromate. After long exposure, gel becomes somewhat difficultly soluble and does no more reset. From this fact, it is probable that the gel changes somewhat in its structure or at least the micelle of gelatine suffers some changes.

The author conceives, from these facts, that at first the gelatine reacts with potassium dichromate on exposure to light and changes to insoluble modification. This modification has a less protective action from crystallisation of silver chromate than before. So the bands become closer and the number of them increases.

Blair, studied the effect of visible light by the exposure to the radiation from a half watt lamp, instead of sun light, at very short distance (6 in. range), and recognised that the bands become irregular. In writer's opinion, by the radiation from a short distance as in Blair's experiment, the energy of light delivered to the gel system does not distribute equally as in the case of parallel ray as sun light. Hence the irregular bands were formed.

According to Blair, ultra-violet ray from quartz mercury lamp makes the formation of bands impossible even in a few hours, while Cluzet and Kofmann found that the formation of Liesegang rings was retarded by ultra-violet light. The retardation of formation of rings is also recognised by the author's experiment. And rings became finer and closer each other than in the non-illuminated case.

Recently Köhn and Mainzhausen[24] have published an interesting results on the influence of light. According to their result, the influence

(23) Cluzet and Kofmann, *Compt. rend. soc. biol.*, **104** (1931), 1001.
(24) Köhn and Mainzhausen, *Kolloid-Z.*, **79** (1937), 316.

of light is recognised when a photo-sensitive substance such as silver chloride is formed in the gel. Subsequently, the author has repeated the experiment on the influence of light that was reported in formerly published work using the gelatine purified by the method of Loeb.[25] Most impurities in gelatine were desorbed, and it was verified by Lüppo-Cramer's method.[26] The gelatine thus purified was almost perfectly free from chlorine or other halogen ions. The obtained results were the same with the former one. The number of bands formed was increased according to the time of exposure to light before superposing the diffusing electrolyte, and the intervals between them became short. It seems that the variation of the distance between bands and the number of them have no concern with the content of chlorine or halogen ions. It gives a very important suggestion on this problem whether rhythmic precipitate of chromate of any metal which does not form a photo-sensitive salt, are affected or not by the irradiation of light. The effect of light on barium chromate bands was studied using the purified gelatine. In this case, the effect of light is also considerable. The experiment was done as follows: a 3% gelatine gel containing 0.5% potassium dichromate as the inner electrolyte was allowed to set in three test tubes in a dark place. The first tube was exposed to direct sun light for about two hours, the second kept in an ordinary room for a day, and the third kept in the dark throughout. A 1 N barium chloride solution was poured on the gels and all three tubes were kept in the darkness. In the test tube exposed to direct sun light the bands became close and blurred and in the test tube kept in diffused light the bands also became close but each band was distinguishable.

Analogous results were also obtained by the influence of ultra-violet ray which is shown in Fig. 8. A gelatine solution which was prepared as above described, was poured into three test tubes of fused silica. One was exposed directly to a quartz mercury lamp, the other exposed to ultra-violet ray filtered from visible rays by a special filter, and the last kept in the dark throughout. The lamp used for this experiment was "Acme"mercury quartz lamp which was made by Shimazu factory. Input of the current applied to the apparatus was 110 volts and 10.2 amperes and the distance between the test tubes and the lamp was about 20 cm. In the photograph, the left is one which was exposed directly to the mercury quartz lamp and the middle to ultra-violet ray and the right unexposed one.

According to the author's opinion, the tanning effect of light plays an important rôle in these cases. This is clear from another fact that light has no influence on the rhythmic banding of the system which does not cause the photochemical reaction between medium and inner electrolyte. For example, lead iodate bands in gelatine are not influenced by light when it was experimented in the condition entirely similar to that of the above described silver chromate system. Also, copper chromate bands in a silicic acid gel are not affected at all by irradiation, for silicic acid and potassium chromate do not react photochemically with each other. On the other hand, there are some rhythmic precipitates on

(25) Loeb, *J. Gen. Phisiol.*, **1** (1918), 237.
(26) Lüppo-Cramer, *Kolloid-Z.*, **5** (1909), 249.

the formation of which light has an essential significance. This is the case, for example, with a rhythmic precipitate of gold. Davies[29] has found first that light has an essential effect on the rhythmic banding of gold. The author considered that red-blue-green zones are probably formed by the variation of external irradiation. This assumption was confirmed by the following experiment: To 20 c.c. of a mixture of equal volumes of a 1.158 density sodium silicate solution and 3 N sulphuric acid, it was added 0.8 c.c. of 1% auric chloride. The gel set in a day or two. This gel was kept in a thermostat and covered with a saturated solution of oxalic acid and irradiated with a 60 watt lamp from 50 cm. distance. As oxalic acid diffused into the gel, auric chloride was reduced. The reduced gold was scattered uniformly, but in transmitted light, many bands could be distinguished in the red violet coloration of colloidal gold. These bands may be formed either by the variation of the light intensity or by the true periodic precipitation. Experiment was done under the irradiation of constant light intensity, which was obtained by using accumulators of large capacity as an electric source. By the continuous irradiation of lamp which was supplied by a current from the accumulators, colloidal gold was separated out and scattered uniformly, and no band was observed in it. So it must be referred to the fact that the bands formed by irradiation with the lamp, are produced by the variation of the intensity of light. A rhythmic precipitate of gold differed from so-called Liesegang ring which is formed by the periodic precipitation of entirely chemical cause, and is only a reflex of external rhythms.

The Effect of Temperature. It is reasonable that the solubility of a precipitate and the diffusion velocity of reactants are affected by temperature. The formation of a rhythmic precipitate on which the solubility and the diffusion velocity have a serious influence, may also be affected by the temperature. In many cases, the lower the temperature is the larger the number of bands formd, and the smaller the intervals between the bands, if the conditions are kept constant excepting temperature. For example, rhythmic precipitates such as silver iodate, silver arsenite and lead iodate in gelatine gels are the cases. The results are shown in the following tables (Table 16–18). Nevertheless, in certain

Table 16.
Band of Silver Iodate.

Temperature (°C.)	Total number of bands	Number of bands*
5	18	12
13	18	10
18	20	6

Inner electrolyte: silver nitrate 0.13%.
Outer electrolyte: potassium iodate 5%.
Gelatine 2.8%.

Table 17. Bands of Silver Arsenite.

Temperature (°C.)	Number of bands**
5	16
13	14
18	13

Inner electrolyte: sodium arsenite 0.67%.
Outer electrolyte: silver nitrate 5%.
Gelatine 4.0%.

Table 18.
Bands of Lead Iodate.

Temperature (°C.)	Number of bands*
5	20
15	15
20	13

Inner electrolyte: potassium iodate 0.4%.
Outer electrolyte: lead acetate 0.5 mol.
Gelatine 2.0%.

(27) Davies, *J. Am. Chem. Soc.* **44** (1922), 2700; *ibid.*, **45** (1923), 2261.

rhythmic precipitates the inverse results were obtained, i.e. the higher the temperature is, the smaller the intervals between bands become. Examples of this case are the rhythmic precipitates of silver carbonate and magnesium hydroxide in gelatine. In the case of silver carbonate, the experiment was carried as follows: sodium carbonate was dissolved in a concentration of 0.17% in 2.5% gelatine and a 5% solution of silver nitrate was placed on it as an outer electrolyte. The experiments were made at 5, 13, and 18°C. In these experiments, the number of bands formed were the same, as shown in Table 19, but in the samples at lower temperatures, the intervals between bands became wider. Popp found that the distance between bands of magnesium hydroxide in gelatine increased as the temperature was lowered.[18] The effects of temperature on the bands differ in case to case, which may be principally caused by the degree of change of diffusibilty of ion and solubility of the formed precipitate. On the whole, the diffusibilities of ions increase with temperature and it seems that the degree of change of diffusibility are not so great and almost of the same extent with various ions, while the difference of degrees of solubility change has a serious significance. The changes of solubilities of the above mentioned substances with temperature are tabulated in the following.

Table 19.

Bands of Silver Carbonate.

Temperature (°C.)	Number of bands
5	7
13	7
18	7

Inner electrolyte: sodium carbonate 0.17%.
Outer electrolyte: silver nitrate 5%.
Gelatine 2.5%.

Table 20.

Silver Carbonate.

Temperature (°C.)	Solubility (mol./l.)
15	1.18×10^{-4} [28]
25	1.16×10^{-4} [29]

Table 21.

Magnesium Hydroxide.[30]

Temperature (°C.)	Solubility (%)
15.5	2.8×10^{-2}
100	4.0×10^{-3}

The solubility of silver carbonate is almost unchanged by the variation of temperature, while that of magnesium hydroxide decreases as temperature is elevated. In general, however, the solubilities of solids increase with the rise of temperature. So, the increase of solubility causes a rhythmic precipitate of large intervals. When the solubility does not change with the change of temperature, the effect of the change of diffusibility is recognised.

(28) Kremers, *Pogg. Ann.*, **85** (1852), 42.
(29) Spencer and M. le Pla, *Z. anorg. Chem.*, **65** (1909), 11.
(30) Fyfe, "Gmelin Handbuch der anorganischen Chemie", II 1, 429.

The author pointed in the foregoing paragraphs, that there are rhythmic bands which are caused by the rhythmical irradiation of light. Similarly, there are bandings which are caused by the rhythmical change of temperature. So-called diurnal bands are made by the rhythms of temperature as well as by those of light. Rhythmic banding of mercuric iodide in a silicic acid gel, which had been presented by Holmes,[31] is an example of such a type. By the author's experiment, it was found that this banding is caused by the rhythmical change of temperature. According to Holmes' description, in a U-tube with a silicic acid gel (obtained by mixing equal volumes of a 1.06 density water glass solution and 1 N acetic acid) filling the bend, 0.5 N mercuric chloride in one arm and 0.1 N potassium iodide in the other, sharp red bands of mercuric iodide followed the curve like ranks of soldiers pivoting in regular formation. The present author noticed, at first that the bands formed are greatly influenced by the weather, and so it was supposed that the bands may be formed by the light. But it was observed that the rhythmic bands have formed even if the U-tube was cut off from any light. Next, the reaction was tried in a thermostat in a dark place, no band was formed and crystals of mercuric iodide were uniformly distributed in the gel. When the U-tube in which the bands were growing, was transferred into a thermostat in a dark place, then the banding has stopped. An example thus obtained is shown in Fig. 9. Diurnal bands are sometimes caused by intermittent light, but many diurnal bands of substances excepting photo-sensitive ones are caused by the change of temperature.

The Influence of the Presence of Impurities or Third Substances. Impurities in gels have often profound influences on the periodic precipitation and the bands formed. It was already pointed that the formed bands are greatly affected by the species of gelatine. This fact is partly referred to the quantities of the species of impurities in the gels. Chlorides and phosphates are contained in the ordinary gelatine as impurities. In the case of silver chromate bands, these impurities form the so-called secondary rhythmic bands by the reaction with silver nitrate. In a gelatine gel which was dialysed and the hydrogen ion concentration regulated adequately, rhythmic precipitates free from secondary bands could be obtained. The secondary band will be treated again in later pages. The existence of a very small quantity of potassium ferrocyanide in gelatine hindered the formation of silver chromate bands and red brown precipitate has deposited uniformly in the gel. The impurities in the gel react with the diffusing electrolyte and form insoluble precipitate which does not form the rhythmic bands. These precipitates hindered the formation of band. For this reason lead iodate, silver arsenite, barium chromate, silver iodate, barium carbonate and lead sulphate are not obtained as rhythmic precipitates in commercial non-dialysed gelatine. The following curious result was obtained in the formation or rhythmic precipitate of lead iodate. A 3% non-dialysed gelatine sol containing previously as much of potassium iodate as to be 1% in concentration was gelatinised and then lead acetate was allowed

(31) H. N. Holmes, *J. Am. Chem. Soc.*, **40** (1918) 1187.

to diffuse into the gel. Continuous white precipitate was formed for the first several days. But a few days later, the first band was formed a little distant from the continuous precipitate. After an interval of one or two days, the second band appeared. When this second band began to appear, the first increased its width and got near enough to touch the continuous precipitate. Then a little later the second band grew and grew, when the first band completely joined the continuous precipitate. When the growth of the second band became prominent, the third began to appear. When the third developed, the second also joined the continuous precipitate. This course was repeated on in order, and finally all the bands were joined into one continuous precipitate. Upon observing this continuous precipitate by holding to a reflective light, it apparently contained the discontinuous parts, which ranged at regular intervals and varied in whiteness.

Therefore, originally, lead iodate must be regarded as to precipitate rhythmically in gelatine. But this result seems to be ascribable to the presence of impurities of such a kind as to produce a white precipitate, probably of phosphate and chloride, by their action on lead ion in the gelatine. It is certified that lead iodate forms a very distinct rhythmic precipitate in a purified gelatine .On the other hand, silver chromate has an entirely different colour from that of silver chloride and silver phosphate which are formed in gelatine by the reaction between impurities and the diffusing electrolyte, silver nitrate. So the bands of silver chromate are formed irrespective of the existence of such impurities.

There are often cases in which the presence of a third substance is favourable for the formation of rhythmic bands. The precipitate of silver chromate becomes very fine in the presence of some potassium citrate, and sharp and thick well-developed bands of orange red colour are observed.[11] This effect, of citrate, is caused by the increase of metastable limit of the solubility of silver chromate in the existence of a salt of polyvalent acid. The author tried to make silver chromate bands in gelatine in the presence of aconitate of the same concentration, being a salt of tervalent organic acid as citrate. Bands have been formed better in the presence of aconitate than in its absence. The particles of silver chromate are fine and bands are sharp and thinner than in the case of the presence of citrate. It is well known that silver chromate does not form bands in agar-agar. Bradford succeeded, however, in obtaining silver chromate bands in an agar-agar gel when the gel contained relatively large quantity of potassium citrate with potassium dichromate. Bradford recommended the following procedure; 2 N silver nitrate solution is allowed to diffuse into a 1% agar-agar gel containing N/100 of potassium dichromate and N/55 of potassium citrate.[8] In the same condition, the author substitute aconitate for citrate and tried to obtain the bands but the trial failed. Accordingly, even if we use an analogous substance, we can not expect the similar results. So it seems that every third substance has its specific effect.

The addition of potassium citrate to the gel is effective for the banding in many examples. When a rhythmic precipitate is indistinct by the deposition of coarse crystals in the interspaces between bands, then the addition of a small quantity of citrate often brings the bands

very distinct. Bands of cobalt phosphate, lead phosphate, silver iodate and lead iodide in silicic acid gels are examples of such cases. It is a well-known fact that when potassium iodide diffuses into a silicic acid gel which contains lead acetate, fern-like fronds grow down into the gel, mixed with many large hexagonal plates. As it was mentioned above, lead iodide makes occasionally a rhythmic precipitate even in silicic acid gel when its crystals are relatively small. We can obtain well-developed bands of lead iodide if there is a third substance which makes the crystals of lead iodide small. Citrate and tartrate are fit for this purpose. Experiments were conducted as follows: At first 0.7–2.0 c.c. of 1 N lead acetate, then 0.05–1.00 c.c. of a 3% solution of potassium citrate were added to a silicic acid gel, which was prepared by mixing 10 c.c. of a 1.06 density solution of water glass and an equal volume of 1 N acetic acid. The gels were prepared in about 100 different conditions. A 2 N solution of potassium iodide was poured on these gels. When both lead acetate and potassium citrate were small in quantity, the separated crystals were relatively coarse and scattered, so that the formation of the bands could not be recognised. When they were large in quantity, a white compound, probably lead citrate, was produced in the sol and precipitated at the bottom of the test-tube. There are, therefore, some limits in adding quantities of lead acetate and potassium citrate. Formation of the rhythmic precipitate was recognised within the limits of 0.4–0.6 c.c. in potassium citrate and of 0.85–1.1 c.c. in lead acetate. The most favourable result was obtained in 0.55 c.c. of potassium citrate and 0.9 c.c. of lead acetate, when 2 N potassium iodide was used as a diffusing electrolyte. Tartrate ion is weaker than citrate ion in the ability of making the crystals of lead iodide finer. Accordingly, in producing the bands of lead iodide by the aid of tartrate ion, a relatively large amount of the ion should be mixed. But in the presence of a large amount of tartrate ion, it produces white precipitate by acting on the ion in the sol. There is naturally some limit in its use. A 2 N solution of potassium iodide was diffused into gel, which was prepared by adding 1.2 c.c. of a lead acetate solution (1 N) and 0.8 c.c. of 3% tartaric acid to a sol prepared by mixing 10.c.c. of sodium silicate solution (d = 1.06) and an equal volume of acetic acid (1 N). In this case the most favourable result could be obtained. In comparison with the case of citrate ion, the crystals were coarse, which stood close and formed thin bands. In Fig. 10, the left shows a typical precipitate, fern-like fronds, of lead iodide in silicic acid gel, the middle a rhythmic precipitate occasionally obtained and the right a rhythmic precipitate in gel containing citrate.

In a preceding communication, the author already reported that the presence of a small quantity of some alcohols, fatty acids or amino acids has a considerable effect on the formation of silver chromate bands.[32] The formation of bands was often strongly inhibited by the presence of a small quantity of fatty acids. The number of bands generally increases in the presence of alcohol but decreases in the presence of amino acids such as glycine and alanine. Koenig[33] pointed out that the

(32) Isemura, this Bulletin, **9** (1934), 236.
(33) Koenig, *J. Phys. Chem.*, **24** (1920), 466.

diffusion and the solubility of the reaction product are so affected and consequently the rhythmic precipitate in a silicic acid gel is also profoundly influenced when alcohols, urea or sugars were added to the gel. When a small quantity of some salts such as potassium iodide or potassium bromide was added to a gel containing soluble phosphate and calcium nitrate was diffused into the gel, a rhythmic precipitate of calcium phosphate in the silicic acid gel will be obtained. In this case, the first four or five bands, consisting of relatively large crystals, were apart but the following bands were blurred, for the crystals were too coarse. The coarseness of the crystals are caused by the fact that the solubility of calcium phosphate is increased in some salts solutions. At the upper part of the gel the ion which forms a rhythmic precipitate is in excess, so the precipitation occurs easily. But, at the lower part of the gel, the small difference of the solubility will largely affect the separation of precipitate. In general, the crystals separate more slowly from more soluble media and the size of the crystals are large. It seems that this is the cause of indistinctness and irregularity of the bands.

In the case of the experiments on the rhythmic precipitation in a silicic acid gel, the gel is usually prepared by mixing a solution of water glass with some acid, and it is used without dialysis. Such a gel always contains a sodium salt of the acid which is formed on the double decomposition of sodium silicate by the acid. These salts as a third substance may have a profound influence on the banding. According to Holmes, the gel which was prepared by mixing a solution of sodium silicate with sulphuric acid, is adequate to the bading of gold but the gel prepared by mixing a solution of water glass with hydrochloric acid or acetic acid is inadequate to the same purpose. The present author, however, obtained good gold bands in the gel prepared by hydrochloric or acetic acid. The appearance of bands is somewhat different from the gel prepared with sulphuric acid.

Holmes said that bands of mercuric iodide are blurred in the presence of chlorine ion, so the use of hydrochloric acid is inadequate to prepare the gel for the formation of those bands. In this case, the gel which was prepared by mixing water glass with acetic acid is adequate. In the case of a rhythmic precipitate of silver chromate in a silicic acid gel, the best developed bands were formed in the gel prepared by mixing water glass with nitric acid. These facts may be considered as the influence of a third substance which is indifferent to the reaction.

Bismuth chromate banding is obtained, when bismuth chloride was forced to diffuse into a silicic acid gel which was prepared by mixing water glass solution with hydrochloric acid. Fig. 11 shows such bands. If the gel was prepared by mixing water glass with acetic acid, bands are difficult to obtain. When bismuth nitrate is allowed to diffuse into the gel prepared by mixing water glass with hydrochloric acid, no band can be obtained. In this case coarse globular precipitate, probably of bismuthy chloride is deposited. In the gel prepared from water glass and acetic acid, on the contrary, a well-developed banding is obtained, while its appearance is quite different from that of the banding by the diffusion of bismuth chloride. This is another example of the fact that a third substance has an important significance on the formation of rhythmic bands.

The Effect of Ageing. It is interesting that the banding is affected with the age of jellies before superimposing the diffusing electrolyte. Schleussner[34] recommended to keep a gelatine gel for twenty four hours before pouring the diffusing solution. The most remarkable observation which has ever been done, is that of Scott Blair.[22] He has made measurements which show that the distance of the last bands from the upper end of jelly increases regularly with the age of gel. This result has been reproduced by the present author.

The author has found another interesting fact. The effect of ageing on the formation of bands did not appear if the experiment was carried as follows. The gelatine solution was prepared and poured into several test-tubes and allowed to set. Then, after different time intervals, each of the test-tubes excepting one, was warmed, melted the gel and allowed again to reset. In this manner, the gels of different age were prepared. Then silver nitrate solution was poured on them. In this case, the formed bands in the respective tubes appeared quite equal and identical to that of unmelted gel, i.e. the most aged gel. From these results the author concludes that the ageing effect of gel on the formation of Liesegang rings is not caused by the change of structure of gel as Scott Blair considered, but by the change of modification of gelatine into less protective one by an interaction of potassium dichromate and this change proceeds with the age. It is considered, moreover, that the decrease of potassium dichromate after ageing was not recognised as Scott Blair observed, for this change of modification is probably caused by spending very small amount of potassium dichromate.

The effect of ageing was also studied on the system of copper chromate in silicic acid gel within the range of three months. The remarkable results as in the case of silver chromate was not seen. According to Koenig,[33] a fresh silicic acid gel gives best bands while the gel kept before diffusion gives irregular results. In the author's experiments on copper chromate, however, even the three months aged gel also gave good regular bands and showed no essential difference from that in a freshly prepared gel.

Subsequently, the author's view was confirmed by some other experiments. The effect of ageing was tested with a rhythmic precipitate in a gel which does not react with the inner electrolyte. Lead iodate bands in a gelatine gel and calcium phosphate bands in a silicic acid gel were investigated. The sol containing the adequate concentration of the inner electrolyte was poured into several test tubes. Then the test tubes were kept in a thermostat. After the gel set, the diffusing electrolyte was superposed on the gel in one of the test tubes. After a while, the diffusing electrolyte was poured on the gel of the second test tube and later on the gel of the third, and so on. After the outer electrolyte had diffused to the bottom of the test tubes, the formed rhythmic precipitates were compared with each other. No recognisable differences were observed. Thus, when the inner electrolyte does not react with the gel, the effect of ageing of gel is not recognisable, so that the effect of ageing is not referred to the change of structure of gels by age.

(34) Schleussner, *Kolloid-Z.*, **31** (1922), 347.

The Influence of the Hydrogen Ion Concentration. In general, the solubility of a salt is considerably influenced by the hydrogen ion concentration of the solution. In many cases, its solubility increases with the hydrogen ion concentration of the medium. It is considered that the Liesegang's phenomenon will be strikingly affected by the hydrogen ion concentration of the gel, because the solubility of the salt is an important factor in the formation of rhythmic precipitates and for the formed bands. However, in many experiments which were hitherto conducted by many investigators, little attention was paid to the hydrogen ion concentration. In view of this point, the author studied thoroughly the influence of hydrogen ion concentration of the medium.

First, silver chromate bands in gelatine was tested. It is well known that the rhythmic precipitate of silver chromate is well developed in an ordinary commercial gelatine. When a small quantity of alkali is added to the gel, the intervals between bands become short and the number of formed bands increases. Inversely, when a small quantity of acid is added in the gel, the intervals between the bands become large, the bands consist of relatively coarse precipitate and have often imperfect appearance and the number of formed bands decreases. On the other hand, the well-developed bands of silver chromate are difficult to obtain in a gelatine which was purified by dialysis. Also it is difficult to obtain in a gelatine of the highest quality. These facts are ascribed by Liesegang[35] to the presence of gelatose, the hydrolytic product of gelatine in an ordinary commercial gelatine. But in the author's opinion, the concentration of hydrogen ion in gelatine jelly is a more significant factor than the presence of gelatose. Ordinary commercial gelatines have the *p*H ranging from 5.5 to 6.4, but pure dialysed gelatines have the *p*H ranging about its isoelectric point that is about 4.7. Accordingly, the author considered that the hydrogen ion concentration of the gel is rather more important than the presence of gelatose. In the jelly which was prepared with "gelatine alba pulvis" from Merck, well-developed bands of silver chromate were formed. But in the jelly which was prepared with the ash-free gelatine (the same gelatine purified by Loeb's method), no bands or only two or three imperfect bands were obtained. However, if a small quantity of caustic soda is added to thus purified gelatine, silver chromate bands were again obtaind in such a gel. When too much alkali was added, the bands became close to each other and blurred. A result of a series of experiments with purified gelatine is shown in Table 22. Table 23 is a result of a series of experiments with purified gelatine, the manufacturer of which is unknown. These cases give coincident results. The bands are formed best at the *p*H range of 5.5–6.0. When the influence of the species of gel on the banding was described in the preceding paragraphs, it was pointed out that the banding is markedly affected by the species of gelatine. The author measured the values of *p*H of those gelatines in its 3% solutions. The results are shown in Table 24. The formation of band, however, can not be referred only to the *p*H of gelatine. Because the band are not the same, even in the same *p*H with different gelatines. The *p*H of the photographic gelatines was also

(35) Liesegang, *Z. physik. Chem.*, **88** (1914), 1.

measured and shown in Table 25. With these gelatines, rhythmic precipitates were easily obtainable in the range of *p*H which is somewhat larger than the preceding examples.

Table 22.

Bands of Silver Chromate.

Sodium hydroxide (0.25 N) added (c.c.)	Number of bands
0.00	4
0.10	16
0.20	27
0.30	39

Inner electrolyte: potassium dichromate 0.15%. Outer electrolyte: silver nitrate 5%. 3.2% gelatine 7 c.c.

Table 23.

Bands of Silver Chromate.

Sodium hydroxide (0.25 N) added (c c.)	Number of bands
0.00	0
0.10	10
0.15	12
0.20	26
0.25	32

Inner electrolyte: potassium dichromate 0.15%. Outer electrolyte: silver nitrate 5%. 3.0% gelatine 7 c.c.

Table 24.

Species	*p*H
Home production A	6.40
Home production B	6.30
Coignet A	5.75
Coignet D	5.55
Coignet No. 1.	5.60

Table 25.

Species	*p*H
Gelatine A for pos. film	5.90
Gelatine B for pos. film	6.30
Gelatine C for pos. film	5.90
Gelatine A for neg. film	5.95
Gelatine B for neg. film	5.65
Gelatine C for neg. film	6.50
Gelatine D for neg. film	5.70

Barium chromate bands in gelatine are greatly influenced by the hydrogen ion concentration. When a cobalt acetate solution was diffused into a gel containing a small quantity of trisodium phosphate as an inner electrolyte, rhythmic precipitate of cobalt phosphate in gelatine are formed while no band is formed in a gel containing secondary sodium phosphate. This fact is also ascribed to the effect of hydrogen ion concentration.

In a gel of organic colloid, such as gelatine, *p*H value of the gel is in a narrow range, if some acid or alkali is not added to the gel. But in the case of a silicic acid gel, *p*H value of the gel will vary widely by the quantities of acid and water glass, which were used to prepare the gel. Accordingly, it seems that the effect of the hydrogen ion concentration on the rhythmic banding in a silicic acid gel is still more remarkable than in the case of gelatine gel. Holmes showed that rhythmic precipitates of copper chromate and basic mercuric chloride are formed in somewhat basic gels of silicic acid. The basic gel contains, in

general, some undecomposed sodium silicate in a small extent. When a solution of a salt of heavy metal diffuses into such a gel, it reacts with undecomposed sodium silicate and forms precipitate of silicate of the heavy metal. There deposits such a precipitate of silicate side by side with the precipitate that forms the rhythmic bands. For example, silver chromate bands in a silicic acid gel are the case. It has long been considered that silver chromate does not make rhythmic bands in the silicic acid gel. This must be ascribed also to the effect of hydrogen ion concentration. In the gel of relatively low hydrogen ion concentration, silver silicate is formed side by side with silver chromate and often hinders the rhythmic handing. When the hydrogen ion concentration is high, the silicic acid does not set to a gel. So the range of hydrogen ion concentration favourable for the formation of typical rhythmic bands is very narrow which has been already pointed out by the present author.[10]

Table 26 shows the results obtained in the gels which have been made by mixing equal volumes of sodium silicate solution (density = 1.06) and nitric acid of different concentrations. With more concentrated nitric acid than 0.70 N, the silicic acid does not gelatinise.

Table 26. Silver Chromate Bands in Silicic Acid Gel.

Concentration of HNO_3 (N)	Nature of rhythmic bands
0.67	Typical rhythmic precipitates consisting of relatively coarse crystals of red black plates were obtained. The intervals between bands were large.
0.63	Typical rhythmic precipitates were obtained. Crystals were small needles.
0.58	At the top of the gel Liesegang bands accompanied by dendrites were recognised. In the middle, only dendrites were seen, and at the bottom again rhythmic bands appeared but they were those formed by diurnal cause.
0.55	The result was analogous to the case of 0.58 N. But the number of formed Liesegang bands was less.
0.50	No Liesegang band was formed. Dendrites and diurnal bands were seen.

Outer electrolyte: $AgNO_3$ 5%. Gel: 6.0 c.c. of Na_2SiO_3 solution (d = 1.06)+6.0 c.c. of HNO_3+0.4 c c. of 5% $K_2Cr_2O_7$ as inner electrolyte.

It is desirable that the gel prepared with plenty of acid, is dialysed thoroughly, though it accompanies some difficulties in addition of the inner electrolyte. In many experiments which were carried out by the present author, the gel which was prepared by mixing equal volumes of a sodium silicate solution (d = 1.06) with 0.7 N nitric acid, 0.7 N sulphuric acid or 0.75 N acetic acid, was favourable for various bandings. The author[36] reported, previously, the banding of nickel dimethylglyoxime in a silicic acid gel. It was studied in the gels of the value of pH ranging

(36) Isemura, *J. Chem. Soc. Japan*, **57** (1936), 546.

from 3.90 to 8.00. The rhythmic precipitate was formed in the *p*H range between 4.80 and 6.40. Relatively long needles were formed in the region of the *p*H value below 4.80, while very minute crystals were formed continuously and no bands were obtained in the region above 6.40. The crystals were large, the thickness of every band was also large and the number of formed bands was small in the lower *p*H region between 4.80 and 6.40. On the contrary, in the higher *p*H, crystals formed were minute, bands were sharp and thin, the number of band was large and the intervals were narrow.

How was the banding influenced, in a silicic acid gel, when the bands were formed as tablets instead of bands consisting of relatively large crystals? On this problem, bands of calcium phosphate were investigated.[7] The results obtained on this rhythmic precipitate are tabulated in Table 27. As shown by this table, it was found that the rhythmic

Table 27. Calcium Phosphate Bands in SilicleAcid Gel.

Concentration of acetic acid (N)	*p*H of gel	Number of bands
0.60	8.98	A continuous precipitate
0.70	7.72	A continuous precipitate
0.75	7.04	9
0.80	6.01	7
0.90	5.50	4
1.00	5.30	3
2.00	4.67	0

Outer electrolyte: $CaCl_2$ 30%. Inner electrolyte: Na_2HPO_4 0.4%. Na_2SiO_3 ($d = 1.06$).

Equal volumes of Na_2SiO_3 and acetic acid were mixed to make a gel. As much of the gel was taken as to fill to a height of 6 cm. of a test tube of 1.2 cm. internal diameter and 11 cm. in length.

precipitate of calcium phosphate could be formed in the range of *p*H between 5.30 and 7.04. The precipitation of calcium phosphate was difficult below 5.30, while the precipitation occurred continuously and no band was formed above 7.04. In the range between 5.30 and 7.04 the smaller the value of *p*H is, the larger the intervals between bands and the smaller the number of formed bands becomes. The distance between the surface of gel and the last formed band becomes large with the value of *p*H of the gel. That is to say, the higher the acidity of the gel is, the more difficult the banding is.

Besides these, the formation of many other rhythmic precipitates, especially such as copper iodate etc., in silicic acid gel were strongly affected by the hydrogen ion concentration. The effect of the concentration of acid which was used to prepare a gel, to the banding was studied, and the results will be given in Part V in this paper.

The hydrogen ion concentration of the diffusing electrolyte as well as that of the gel, has also a profound influence on the rhythmic pre-

cipitation. On the formation of rhythmic bands of bismuth chromate, the bismuth nitrate solution in nitric acid of various concentration was used as the outer electrolyte. With bismuth nitrate in diltue nitric acid, bands were formed from the top of gel; the number of them was large and the interspaces between them were very small. On the contrary, with bismuth nitrate in concentrated nitric acid, the band was not formed at the top of the gel but appeared at a certain depth from the surface. The number of formed bands were small and interspaces between them were large. The distance from the top of the gel to the first formed band was increased with the concentration of nitric acid. The distance to the last formed band from the surface of the gel was also increased with the concentration of nitric acid. These results are all referred to the increase of solubility of formed bismuth chromate with increasing acidity.

III. Regularity of the Intervals Between Bands.

It is an established fact that in the Liesegang phenomenon the intervals between bands become larger as the distance increases from the contact surface with the outer electrolyte solution. Schleussner[37] said that the interval of the nth band and that of the $(n+1)$th band stood in a constant ratio. The author[38] experimentally proved that the intervals of bands beared a relation of a quadratic equation to the numbers of the formed bands. When the interval of nth band is shown by ΔX_n, we can obtain as equation.

$$\Delta X_n = a + bn + cn^2 \qquad (1)$$

in which a, b and c are constants.

Bauer,[39] supposing that an equation of the same form as the partial differential equation of heat conduction could be applied in the diffusion of ion into a gel, set up the equation:

$$\frac{\partial u}{\partial t} = a^2 \frac{\partial^2 u}{\partial X^2}$$

where u means the concentration of the ion to diffuse from an external liquid into the gel; t the time; x the interval; and a^2 the diffusion constant. From this equation he theoretically drew a conclusion from the standpoint of super-saturation theory that the ratio of the interval of nth band to that of $(n+1)$th band could be shown by

$$\frac{\Delta X_{n+1}}{\Delta X_n} = 1 + p$$

in which p is

$$\frac{\Delta X}{x^*} \sim \frac{\Delta t}{2t^*} = p \sim \text{const.}$$

(37) Schleussner, *Kolloid-Z.*, **34** (1924), 338.
(38) *J. Chem. Soc. Japan*, **55** (1934), 809.
(39) *Kolloid-Z.*, **64** (1933), 181.

where t^* is the time required to form precipitates and x^* is the distance to the locality where the precipitate is formed.

If the interval between the stopper* and the first band is shown by ΔX_0, we can obtain and can set up in order

$$\frac{\Delta X_1}{\Delta X_0} = 1+p$$

$$\frac{\Delta X_2}{\Delta X_1} = 1+p$$

$$\frac{\Delta X_3}{\Delta X_2} = 1+p$$

$$\cdots\cdots\cdots$$

$$\frac{\Delta X_n}{\Delta X_{n-1}} = 1+p\,.$$

Multiplication in each side of the equations gives the following relation

$$\frac{\Delta X_n}{\Delta X_0} = (1+p)^n\,.$$

If the right side of this equation is expanded by the binominal theorem, we obtain

$$\frac{\Delta X_n}{\Delta X_0} = \left\{1+np+\frac{n(n-1)}{2!}p^2+\frac{n(n-1)(n-2)}{3!}p^3+\cdots\right\}.$$

As p is a number of small value, we may neglect the higher terms of p and we get

$$\Delta X_n = \Delta X_0\left\{1+np+\frac{n(n-1)}{2}p^2\right\}$$

or

$$\Delta X_n = \Delta X_0+\Delta X_0\left(1-\frac{p}{2}\right)pn+\frac{\Delta X_0}{2}p^2n^2\,. \qquad (2)$$

As ΔX_0 and p are constants, we may denote,

$$\Delta X_0 = a\,, \qquad \Delta X_0\left(1-\frac{p}{2}\right)p = b\,, \qquad \frac{\Delta X_0}{2}p^2 = c\,.$$

Now this equation is identical with the above-mentioned empirical formula

$$\Delta X_n = a+bn+cn^2\,.$$

In Table 28, as an example, the results are shown on the rhythmic precipitate of copper chromate in a silicic acid gel. Second column shows the observed values and the fourth column the values which were obtained by the empirical equation (1), and the fifth column the values

* The word stopper means the german "Propfen" after Popp. (*Kolloid-Z.*, **36** (1925), 208).

which were obtained by the equation (2) in which a, b and c were calculated from the experimentally determined p and ΔX_0.

Table 28. Copper Chromate in a Silicic Acid Gel.

No.	$\Delta X_{obs.}$	$1+p=k$	$\Delta X_{calc.}$ by empir. formula	$\Delta X_{calc.}$ by theor. formula
1	0.09		0.09	0.09
2	0.10	1.11	0.10	0.10
3	0.12	1.20	0.11	0.12
4	0.13	1.08	0.13	0.13
5	0.14	1.08	0.14	0.14
6	0.16	1.14	0.16	0.16
7	0.18	1.14	0.18	0.17
8	0.20	1.11	0.20	0.19
9	0.22	1.10	0.23	0.21
10	0.24	1.09	0.26	0.23
11	0.27	1.13	0.28	0.25
		Average 1.117		

In the empirical formula (1), calculation was made in taking $a = 0.080$, $b = 0.075$, and $c = 0.001$. In the theoretical formula (2), it was made by using the constants a, b and c which were calculated from $\Delta X_0 = 0.083$ and $p = 0.117$. It was ascertained that both formulas gave almost identical values.

Subsequently, the formula was applied on other rhythmic precipitates namely, those of calcium phosphate in silicic acid gel, silver arsenite in gelatine, and lead iodate in gelatine. The distances between bands calculated from the theoretical formula were fairly concordant with the experimental data. But the calulated values of the higher number is always somewhat smaller than observed values.

Table 29 gives the results obtained with calcium phosphate in a silicic acid gel. The values of the fourth column were obtained from the assumption of $a = 0.173$, $b = 0.00241$, and $c = 0.00029$, and those of the fifth column calculated from $\Delta X_0 = 0.176$ and $p = 0.154$.

Table 29. Calcium Phosphate in a Silicic Acid Gel.

No.	$\Delta X_{obs.}$	$1+p=k$	$\Delta X_{calc.}$ by empir. formula	$\Delta X_{calc.}$ by theor. formula
1	0.20		0.20	0.20
2	0.23	1.15	0.23	0.23
3	0.27	1.17	0 27	0.27
4	0.31	1.15	0.31	0.31
5	0.35	1.13	0.37	0.35
6	0.39	1.11	0.42	0.40
7	0.45	1.15	0.48	0.45
8	0 54	1.20	0 55	0.51
9	0.61	1.13	0.62	0.57
10	0.73	1.20	0.71	0.63
		Average 1.154		

Table 30 gives the results obtained with silver arsenite in gelatine, which were calculated on the assumption; $a = 0.083$, $b = 0.0049$, $c = 0.000145$, $\Delta X_0 = 0.083$, $p, = 0.0611$.

Table 30. Silver Arsenite in Gelatine.

No.	$\Delta X_{obs.}$	$1+p=k$	$\Delta X_{calc.}$ by empir. formula	$\Delta X_{calc.}$ by theor. formula
1	0.087		0.087	0.087
2	0.091	1.046	0.092	0.092
3	0.099	1.088	0.098	0.098
4	0.101	1.020	0.104	0.104
5	0.110	1.087	0.110	0.110
6	0.120	1.091	0.117	0.117
7	0.122	1.017	0.123	0.123
8	0.129	1.058	0.130	0.130
9	0.138	1 070	0.138	0.138
10	0.147	1.068	0.146	0.146
11	0.151	1.028	0.153	0.153
12	0.165	1.100	0.162	0.162
		Average 1.0611		

Table 31 gives the results obtained with lead iodate in gelatine, which were calculated on the assumption: $a = 0.132$, $b = 0.01006$, $c = 0.00075$, $\Delta X_0 = 0.131$, $p = 0.096$.

Table 31. Lead Iodate in Gelatine.

No.	$\Delta X_{obs.}$	$1+p=k$	$\Delta X_{calc.}$ by empir. formula	$\Delta X_{calc.}$ by theor. formula
1	0.143		0.143	0.144
2	0.156	1.189	0.155	0.157
3	0.168	1.078	0.169	0.172
4	0.180	1.070	0.184	0.189
5	0.201	1.116	0.201	0.206
6	0.218	1.085	0.219	0.225
7	0.232	1.064	0.239	0.244
8	0.254	1.095	0.260	0.265
9	0.281	1.107	0.283	0.286
10	0.325	1.157	0.308	0.311
		Average 1.096		

As seen from these four tables, the values of ΔX obtained by the empirical formula and those calculated from the theoretical formula are in good concordance.

IV. Classification and Secondary Bands.

Classification of Rhythmic Precipitates. Among the banded precipitates which are known commonly as rhythmic precipitates, some are produced by different causes from that of the so-called Liesegang phenomenon. So, the rhythmic precipitates can and must be arranged at least into the following three classes.

(1) Rhythmic precipitate as a Liesegang phenomenon.
(2) Rhythmic precipitate as the reflex of external rhythms.
(3) Compound rhythmic precipitate.

Silver chromate bands in gelatine are a typical Liesegang phenomenon. Many rhythmic precipitates such as lead iodate, magnesium hydroxide, silver carbonate in gelatine, copper chromate, calcium phosphate in silicic acid gel, etc. belong to this type. By the aspects of the bands formed, this class can be further divided into two sub-classes. These two sub-classes have been indicated as the two classes of rhythmic precipitate by Chatterji and his collaborators,[40] the classification of which is based on the shape and not on the nature. The classification based on structure will be described later.

A rhythmic precipitate formed as the reflex of external rhythms may be obtained in many precipitating reactions. It is caused by the change of diffusion velocity or by the furtherance and the hindrance of precipitation by external rhythms. External rhythms occur naturally with the change of day and night, which brings the periodical change of light and temperature. For example, the rhythmic banding of gold is caused by the rhythm of light intensity while that of mercuric iodide in a silicic acid gel is produced by the rhythm of temperature. The characteristic of this type of rhythmic precipitate is that one band is formed by one rhythm and that the intervals between bands become smaller with the advance of band formation. It is because diffusion velocity becomes gradually slow that the intervals become smaller. At the bottom of the gel, the inner electrolyte is exhausted and the intervals between bands become large again. Accordingly, rhythmic precipitates made by external rhythms often have minimum intervals between bands in the lower part of the gel.

In a rhythmic precipitate of gold, there exists several secondary bands which are caused by the change of intensity of irradiation. A band always consists of red-violet-blue-green-yellow zones. This fact is connected with the change of light intensity of morning, noon and evening.

Compound rhythmic precipitate is the one composed of true Liesegang phenomenon and the rhythmic precipitate of diurnal causes. For example, lead iodide in a silicic acid gel containing a small quantity of citrate formed often this type of rhythmic precipitate. In this case diurnal black bands caused by the partial decomposition of lead iodide by light and diurnal bands caused by the change of temperature were

(40) Chatterji and Dhar, *J. phys. Chem.*, **28** (1924), 41; *Kolloid-Z.*, **40** (1926), 97; Mukherjee and Chatterji, *Kolloid-Z.*, **50** (1930), 147.

formed in addition to a rhythmic precipitate as a Liesegang phenomenon. These three banding appeared simultaneously. This is a good example of compound rhythmic precipitate.

Rhythmic precipitates may be classified according to the structure as follows:

(1) Banded precipitate (or Liesegang rings)
Sub-class I
Sub-class II
(2) Helicoidal precipitate. (or spiral precipitate)
(3) Banded precipitate with bands of saturn structure.
(4) Radial precipitate.[41]
(5) Complicated modification.

Ordinary rhythmic precipitates form bands in test tube, while they form rings on glass plate. This class may be divided into two subclasses: I, the tablet-like bands separated by marked gaps or empty spaces and II, the rhythmic precipitate of the type which has deposition maxima. In the former the precipitate is often paste-like, but in the latter, it is often well-defined crystals. As examples of type I, we can indicate calcium phosphate in silicic acid gel and magnesium hydroxide in gelatine, and as an example of II type, lead iodide in silicic acid gel.

A helicoidal precipitate is obtained in a test tube, while a spiral precipitate is obtained on a glass plate. If the diffusing electrolyte is superposed on a gel before it sets firmly enough, a helicoidal precipitate is often formed. So, it is closely connected with the deformation of the gel, which is mechanically caused by the addition of the diffusing electrolyte. Bands of saturn stucture are, of course, obtained only in a test tube, while a radial precipitate is obtained on a glass plate. It seems, the formation of bands of saturn structure depends on the ease of precipitation along the glass wall and active diffusion in the center of the test tube. Other forms of band are special cases. These can be included in the complicated modifications.

Secondary Bands. When a rhythmic precipitate of silver chromate is formed in gelatine, many thin faint layers are usually observed in the interspaces between brick red bands of silver chromate. These layers are known as secondary bands, and ascribed, by Köhler,[42] to the rhythmic precipitation of ammonium nitrate or potassium nitrate which is formed by the interaction of ammonium dichromate or potassium dichromate and silver nitrate. On the other hand, Schleussner[43] insists that these secondary bands are caused by silver chloride or phosphate which is formed by the interaction of the diffusing silver nitrate and chloride or phosphate contained in gelatine as an impurity. The author support Schleussner's consideration from the standpoint of the following experiments.

(41) Veil, *Compt. rend.*, **196** (1933), 1491.
(42) Köhler, *Kolloid-Z.*, **19** (1916), 65.
(43) Schleussner, *Kolloid-Z.*, **31** (1922), 347.

When silver nitrate solution is allowed to diffuse into gelatine without any inner electrolyte, then there are obtained a number of thin bands. In this case the bands must consist of silver salt, for such a soluble salt as potassium nitrate or ammonium nitrate is generally difficult to obtain in a rhythmic precipitate. It is interesting that with increasing *p*H the intervals between silver chromate bands decrease but the intervals between secondary bands increase. This change of the intervals of secondary bands with *p*H is inverse to the cases of general rhythmic precipitates. In gelatine without chromate, however, the intervals between secondary bands decrease with increasing *p*H. So, it seems that in gelatine of large *p*H, more silver ion is consumed by the precipitation of silver chromate bands, and in such a gel, the secondary bands have larger intervals because silver ion decreases and the result obtained is exactly the same as by the decrease of concentration of the diffusing electrolyte.

The author experimented on the formation of silver chromate bands with gelatines which were dialysed in different degrees. In the less dialysed gelatine, the number of the secondary bands formed is large and the intervals between them are small, but in well-dialysed gelatine, the number of secondary bands is small and the intervals between them become large.

V. Special Part.

Conditions for the Formation of Some New Examples. In the course of the present study, the author found many new examples of rhythmic precipitates. Some detailed description of these examples will be given in the followings. Conditions for banding have also been investigated of some rhythmic precipitates which were hitherto reported by other authors giving no detailed description. Among the following experiments, those with bismuth chromate, bismuthyl chloride, bithmuthyl nitrate, calcium phosphate, and lead iodide in silicic acid gel were conducted in the test tubes of internal diameter of 1.5 cm., while the other experiments were all conducted in the test tubes of internal diameter of 1.2 cm.

Barium Chromate in Gelatine Gel. When a solution of barium chloride was poured on a pure ash-free gelatine jelly containing potassium dichromate as the inner electrolyte, bands were obtained of pale yellow relatively coarse particles of barium chromate. It is remarkable that these bands formed only in purified gelatine, but not in ordinary non-dialysed gelatine. This may be explained by the fact that the impurities contained in gelatine react with barium chloride and form insoluble salt distributing uniformly in the gel and prevent the band formation of barium chromate.

In the test tube the gelatine jelly is dehydrated, probably, by the tanning action of barium chloride and the meniscus of the jelly is depressed in the centre. Accordingly every band has remarkably concave form in its central part. At the top of the gel the bands are thin, but in the lower part of the gel they are thick consisting of relatively large

crystals. The conditions for the banding are summarised in the following table. In this table, the 1st column expresses the number of experiment, the 2nd, the volume of 3.2% gelatine solution, the 3rd, the water added to the gelatine to make the definite volume of gel, the 4th, the inner electrolyte, and the 5th, the added alkali.

Table 32.

No.	Gel				Outer electrolyte	Results
	Gelatine solution (3.2%) (c.c.)	Water added (c.c.)	$K_2Cr_2O_7$ solution (5.0%) (inner electrolyte) (c.c.)	NaOH solution (1.0%) (c.c.)		
1	5.00	0.00	2.00		$BaCl_2$ 1 N	Diffused bands.
2	5.00	1.00	1.00		,,	
3	5.00	1.50	0.50		,,	Typical rhythmic bands.
4	5.00	1.90	0.10		,,	Some faint bands.
5	5.00	1.95	0.05		,,	No band formation.
6	7.20	0.30	0.80	0.00	,,	
7	7.20	0 20	0.80	0.10	,,	Well-developed bands.
8	7.20	0.10	0.80	0.20	,,	
9	7.20	0.00	0.80	0.30	,,	

No. 1 and No. 2 gave bands, which were thin and compact at the top of the gel while they became diffuse and they consisted of coarse crystals in the lower part. No. 3 was the most favourable condition and gave typical bands. In No. 4, the concentration of the inner electrolyte was too dilute to form a distinct rhythmic precipitate. Consequently, faint bands have formed only at the top of the gel. No. 5 gave no bands, but a scattered precipitate. From No. 6 to No. 9, there appears the influence of the acidity of the gel. In an acidic gel such as No. 6, the bands consisted of coarse crystals and were somewhat indistinct. The less acidic the gel became, the more easily the precipitation occurred; and the more distinct the bands became, within the extent of the above experiments. As already stated, this banding is strongly affected by the irradiation of visible or ultraviolet light before superposing the diffusing electrolyte.

Lead Carbonate in Gelatine Gel. Lead acetate or lead nitrate solution is diffused into a gel, which has been prepared from gelatine purified by Loeb's method and contains sodium carbonate or ammonium carbonate as the inner electrolyte. Then well-developed rhythmic bands consisting of a somewhat coarse globular precipitate are obtained. In the case of relatively low concentration of the inner electrolyte the bands consisting of crescent shaped fragments are obtained. In gels containing somewhat more concentrated inner electrolytes, bands of saturn structure are often formed. In the presence of a sufficient quantity of inner electrolyte in the gel good typical bands are obtained. Conditions for

the experiments are given in Table 33. The meaning of the data in the table is quite the same with the former table.

In the experiment No. 1 many crescent shaped fragments of bands were formed, which was so incomplete that they were scarcely perceived as a rhythmic precipitate. From No. 2 to No.4, there were many bands of saturn structure in the lower part of gel. No. 5 gave typical bands. As seen from the table (No. 2–No. 7), the number of formed bands in-

Table 33.

No	Gel				Outer electrolyte		Number of bands	Results
	Gelatine solution (3.0%) (c.c)	Water added (c.c.)	Inner electrolyte (c.c.)					
1	5.0	0.6	Na_2CO_3 (5%)	0.4	$Pb(CH_3COO)_2$	1 N		Fragmental bands.
2	5.0	0.5	,,	0.5	,,		12	Bands of saturn structure.
3	5.0	0.4	,,	0.6	,,		15	
4	5.0	0.3	,,	0.7	,,		15	
5	5.0	0.2	,,	0.8	,,		22	Typical rhythmic bands.
6	5.0	0.1	,,	0.9	,,		29	
7	5.0	0.0	,,	1.0	,,		31	
8	5.0	0.6	$(NH_4)_2CO_3$ (5%)	0.4	,,			
9	5.0	0.2	,,	0.8	,,			
10	5.0	0.5	$Pb(CH_3COO)_2$ (1 N)	0.5	$(NH_4)_2CO_3$	5%		Typical bands.
11	5.0	0.5	,,	0.5	Na_2CO_3	5%		

creases with the concentration of the inner electrolyte. No. 8 gave bands consisting of coarse crystals. In this case thin white bands were formed at first, which then converted into bands consisting of coarse crystals. In No. 9 the first four bands were distinct and all convex, but those in the lower part of the gel were blurred. No. 10 and No. 11 gave also typical bands which indicate that the interchange of inner and outer electrolytes gave small influence on the banding. The right photograph in Fig. 12 is an example of this rhythmic precipitate.

Lead Carbonate in Silicic Acid Gel. When lead acetate or lead nitrate solution diffuses into a silicic acid gel containing sodium carbonate as inner electrolyte, lead carbonate bands are obtained. As it was already mentioned in the preceding paragraphs, the rhythmic bands of lead carbonate in gelatine consisted of globular particles. In silicic acid gel, however the bands consisted of relatively long needles, sometimes accompanied by a small amount of globular particles. The length of the needles obtained often attained several millimeters in a gel of somewhat high acidity. The conditions of the experiments are summarised in Table 34.

Table 34.

No.	Gel: Na_2SiO_3 solution (d=1.06) (c.c.)	Gel: CH_3CO_2H solution (c.c.)	Gel: Inner electrolyte (c.c.)	Gel: Water added (c.c.)	Outer electrolyte	Number of bands	Results
1	3 0	0.75 N 3.0	Na_2CO_3 (5.0%) 0.2	0.8	$Pb(NO_3)_2$ 1 N	12	Typical rhythmic bands
2	3.0	,, 3.0	,, 0.4	0.6	,,	14	
3	3.0	,, 3.0	,, 0.6	0.4	,,	26	
4	3.0	,, 3.0	,, 0.8	0.2	,,	36	
5	3.0	,, 3.0	,, 1.0	0.0	,,	45	
6	3.0	,, 3.0	,, 0.6	0.4	$Pb(CH_3CO_2)_2$ 1 N	18	
7	3.0	,, 3.0	,, 0.8	0.2	,,	40	
8	3.0	,, 3.0	,, 1.0	0.0	,,	50	
9	3.0	0.60 N 3.0	,, 0.5	0.5	$Pb(NO_3)_2$ 1 N		Close bands
10	3.0	,, 3.0	,, 0.5	0.5	$Pb(CH_3CO_2)_2$ 1 N		
11	3.0	0.65 N 3.0	,, 0.5	0.5	$Pb(NO_3)_2$ 1 N		
12	3.0	,, 3.0	,, 0.5	0.5	$Pb(CH_3CO_2)_2$ 1 N		
13	3.0	07.0 N 3.0	,, 0.5	0 5	$Pb(NO_3)_2$ 1 N		Typical bands
14	3.0	,, 3.0	,, 0.5	0.5	$Pb(CH_3CO_2)_2$ 1 N		
15	3.0	1.0 N 3.0	,, 0.3	0.7	$Pb(NO_3)_2$ 1 N	1	Only one band was obtained
16	3.0	,, 3.0	,, 0.5	0.5	,,	3	
17	3.0	,, 3.0	,, 0.7	0.3	,,	3	
18	3.0	,, 3.0	,, 0.9	0.1	,,	6	
19	3.0	,, 3.0	,, 1.0	0.0	,,	6	Bands consisted of long crystals
20	3.0	0.75 N 3.0	$Pb(NO_3)_2$ (1 N) 0.3		Na_2CO_3 5.0%	4	Some diffused bands
21	3.0	,, 3.0	$Pb(CH_3CO_2)_2$ (1 N) 0.3		,,	3	

In No. 1. typical rhythmic bands were obtained, which consisted of needles and were separated by large clear interspaces. No. 2 also gave a typical rhythmic precipitate, the crystals of which were distributed more densely. In No. 1–No. 8, the number of bands formed increased with the concentration of inner electrolyte. In No. 3–No. 8, every band that consisted of globular precipitate was sharp at the lower surface on which the needles grew. At the bottom of the gel two or three bands have deposited which were consisted only of globular precipitate. In No. 9, there formed a white continuous precipitate down to the middle part of the gel, while many indistinct bands formed from the middle to the bottom of the gel. They were complicated probably by the formation of lead silicate. In No. 10, at the middle of the gel close bands and at the bottom of the gel distinct ones were formed. The bands did not consist of needles. No. 11 was analogous to No. 9, the bands being more distinct. No. 12 was analogous to No. 10, the bands being also more distinct. Both No. 13 and No. 14 gave typical rhythmic bands. At the middle of the

gel, the bands blurred by the growth of crystals, but at the bottom the bands became distinct again, because the intervals between them increased. In No. 15 only a band was obtained consisting of small globules at 1.2 cm. from the top of the gel. No. 16–No. 18 gave bands similar to those of No. 15, but they consisted of somewhat shorter needles. No. 19, gave bands formed by the cluster of long crystals. No. 20 and No. 21 did not give good bands. In No. 15–No. 19, the effect of the concentration of the inner electrolyte was observed as usual.

It is seen from the foregoing results that a rhythmic precipitate of long crystals is well developed in a gel which is prepared by mixing an equal volumes of a 1.06 density water glass solution with a 0.7 N or more concentrated solution of acetic acid. In a gel which is prepared by mixing equal volumes of a water glass solution ($d = 1.06$) and 0.65 N or less concentrated acetic acid, banding is not good. The appearance of crystals is quite different by the acidity of the gel. This is caused probably by the formation of lead silicate and lead carbonate. In Fig. 12, the middle photograph shows a typical rhythmic precipitate of lead carbonate in silicic acid gel and the left an example of the bands consisting of long needles.

Even if the inner electrolyte is interchanged with the outer electrolyte, the rhythmic bands still formed. But when sodium carbonate or ammonium carbonate is allowed to diffuse into the gel, the bands are not so distinct as the case where the lead salts diffuses into the gel.

Bismuth Chromate in Silicic Acid Gel. When a solution of bismuth nitrate or bismuth chloride diffuses into a silicic acid gel containing potassium chromate as inner electrolyte, yellow bands of bismuth chromate are obtained. The appearance of this rhythmic precipitate is greatly affected by the kind of acid which was used to prepare the gel, by the species of the diffusing electrolyte, and by the acidity of the diffusing solution and of the gel itself. The conditions for obtaining this rhythmic precipitate are shown in Table 35.

In this table, $Bi(NO_3)_3$ I indicates a 0.5 mol solution of bismuth nitrate in 3 N nitric acid, and $Bi(NO_3)_3$ II, a 0.5 mol solution in the least concentration of nitric acid that does not cause hydrolysis. The rhythmic precipitate has better developed by the diffusion of bismuth nitrate than that of bismuth chloride. The solution of bismuth chloride which was used in the present experiments is a 1 mol solution in hydrochloric acid. The rhythmic bands formed by the diffusion of bismuth nitrate were yellow and had many pores in the bands. The precipitate grew at the interface between the glass and the gel, and the bands in the lower part of the gel were cloaked with this yellow film of the precipitate.

When the rhythmic precipitate was made by the diffusion of a bismuth nitrate solution in relatively concentrated nitric acid, the band was first formed at a point somewhat distant from the top of the gel. In No. 1, the first band formed at a point 1.3 cm. distant from the top of the gel; in No. 2, 1.7 cm.; in No. 3, 2.2 cm.; and in No. 4, 2.4 cm. In No. 5–No. 8, only several faint bands formed at the top of the gel, then a globular precipitate uniformly formed and no bands and no precipitate formed from the middle to the bottom. In No. 9–No. 12, we

Table 35.

No.	Gel: Na_2SiO_3 solution (d=1.06) (c.c.)	Gel: Acid (c.c.)	Gel: Inner electrolyte (c.c.)	Outer electrolyte	Number of bands	Results
1	6.5	CH_3CO_2H (0.5 N) 6.5	K_2CrO_4 (1 mol) 1.0	$Bi(NO_3)_3$ I	5	Typical rhythmic precipitates were formed.
2	6.5	,, 6.5	,, 0.8	,,	3	
3	6.5	,, 6.5	,, 0.5	,,	3	
4	6.5	,, 6.5	,, 0.2	,,	3	
5	6.5	,, 6.5	,, 1.0	$BiCl_3$		Faint rhythmic bands were formed.
6	6.5	,, 6.5	,, 0.8	,,		
7	6.5	,, 6.5	,, 0.5	,,		
8	6.5	,, 6.5	,, 0.2	,,		
9	6.5	,, 6.5	,, 1.3	$Bi(NO_3)_3$ II	15	Typical rhythmic bands were formed.
10	6.5	,, 6.5	,, 1.0	,,	18	
11	6.5	,, 6.5	,, 0.8	,,	22	
12	6.5	,, 6.5	,, 0.5	,,	18	
13	6.5	HCl (0.85 N) 6.5	,, 1.0	$BiCl_3$		No bands were obtained.
14	6.5	,, 6.5	,, 1.0	$Bi(NO_3)_3$ I		
15	6.5	,, 6.5	,, 1.0	$Bi(NO_3)_3$ II		
16	6.5	HCl (0.5 N) 6.5	,, 0.5	$Bi(NO_3)_3$ I		
17	6.5	HCl (0.5 N) 6.5	,, 0.5	$Bi(NO_3)_3$ II		
18	6.5	,, 6.5	,, 1.3	$BiCl_3$	2	Well developed rhythmic bands were obtained.
19	6.5	CH_3CO_2H (0.5 N) 6.5	,, 0.5	$Bi(NO_3)_3$ I	6	
20	6.5	,, 6.5	,, 0.5	$Bi(NO_3)_3$ II 2 N HNO_3	6	
21	6.5	,, 6.5	,, 0.5	$Bi(NO_3)_3$ 1 N HNO_3	19	

obtained the best bands. Fig. 13 shows an example of this type of rhythmic precipitate. In No. 13, there formed many large spherulites, but no bands. In No. 14–No. 17, the results were analogous to that of No. 13. In No. 18, a stopper of the precipitate and two large bands, separated by large interspaces formed and these all consisted respectively of secondary rhythmic bands.

Thus the bands which were obtained by the diffusion of bismuth chloride in a gel prepared with hydrochloric acid were quite different to those formed by the diffusion of bismuth nitrate in a gel which was prepared with acetic acid. Fig. 11 shows an example of this type of rhythmic precipitate. This is partly referred to the fact that bismuth chloride hydrolyses more easily than bismuth nitrate. The bands formed by bismuth chloride is always accompanied by bismuthyl chloride. They seemed to be a compound rhythmic precipitate of bismuth chromate and bismuthyl chloride.

In the examples of No. 5–No. 8 and No. 13–No. 17, many globular particles are seen. These are not bismuth chromate but probably bismuthyl chloride. The formation of bismuthyl chloride and bismuthyl nitrate bands in silicic acid gel wil be treated later again. The rhythmic bands of bismuth chromate are never formed by the diffusion of bismuth nitrate into the gel prepared with hydrochloric acid. It has already been stated that when bismuth nitrate diffused into a gel prepared with acetic acid like in the experiments No. 1–No. 4, bands having many pores were obtained. Moreover, the bands often showed the saturn type or more complicated structures. When this rhythmic precipitate are stood for a long time (five to six months), the crystallisation of bismuth chromate occurred, and orange clusters of crystals have deposited by the further advance of the diffusion. With the growth of these crystals the bands began to chip, and crescent shaped bands formed. At last, the bands disappeared entirely and several somewhat large spherical clusters of crystals remained.

Bismuthyl Chloride and Bismuthyl Nitrate in Silicic Acid Gel. The author studied the formation of rhythmic precipitates of bismuthyl chloride and bismuthyl nitrate in silicic acid gel, for bismuth chloride and bismuth nitrate are both readily hydrolysable. When bismuth chloride or bismuth nitrate diffuses into a silicic acid gel which contains no inner electrolyte, a white rhythmic precipitate is formed. The best bands were formed when bismuth chloride is allowed to diffuse in the gel prepared with hydrochloric acid. The conditions for the experiments are summarised in Table 36.

Table 36.

No.	Gel			Results
	Na_2SiO_3 solution (d=1.06) (c.c.)	Acid (c.c.)	Outer electrolyte	
1	7.0	CH_3CO_2H (0.5 N) 7.0	$BiCl_3$	No bands were formed.
2	7.0	,, 7.0	$Bi(NO_3)_3$ I	
3	7.0	HCl (0.5 N) 7.0	$BiCl_3$	Rhythmic bands were formed.
4	7.0	HCl (0.42 N) 7.0	,,	
5	7.0	CH_3CO_2H (0.5 N) 7.0	$Bi(NO_3)_3$ II	

The concentrations of the diffusing electrolyte were the same as in the case of bismuth chromate. In No. 1, a white globular precipitate formed uniformly all through the test tube. In No. 2, there is no band and a small amount of precipitate formed sparsely. In No. 3–No. 5 rhythmic bands were formed. In No. 4 four compact bands and one consisting of globular particles were formed, each band being consisted of far smaller crystals than in the case of No. 3. In No. 5 eight bands were formed, each of which consisted of a small amount of scattered crystals.

From the foregoing results we can conclude that no band is formed in a gel which is prepared by mixing a water glass solution and acetic acid when bismuth chloride is chosen as diffusing electrolyte. Bismuth nitrate is less hydrolysable than bismuth chloride, so when $Bi(NO_3)_3$ I diffuses in a gel there is no band formation. But when $Bi(NO_3)_3$ II diffuses, rhythmic bands form, because $Bi(NO_3)_3$ I is difficultly hydrolysable in an excess of nitric acid.

Cobalt Phosphate in Silicic Acid Gel. When cobalt acetate diffused into a gel containing a small quantity of soluble phosphate as inner electrolyte, a red rhythmic precipitate of cobalt phosphate were formed. Every band was thick while the particles forming the bands were considerably coarse. The bands were not so distinct because the particles forming them were coarse and scattered. When a very small quantity of citrate was added to the gel, well developed bands such as shown in Fig. 14 was obtained. The left photograph is an example of cobalt phosphate bands in a silicic acid gel. The experimental conditions are summarised in Table 37 and the results are given in the following lines.

Table 37.

No.	Gel					Outer electrolyte	Results
	Na_2SiO_3 solution (d=1.06) (c.c.)	Water	CH_3CO_2H solution (1 N) (c.c.)	Inner electrolyte (c.c.)			
1	3.0	0.6	2.4	Na_2PO_4 (0.5 mol)	0.2	$Co(CH_3CO_2)_2$ 10%	Bands consisting of coarse crystals were formed.
2	3.0	0.7	2.3	,,	0.2	,,	
3	3.0	0.8	2.2	,,	0.2	,,	Somewhat indistinct bands were formed.
4	3.0	0.9	2.1	,,	0.2	,,	
5	3.0	1.0	2.0	,,	0.2	,,	
6	3.0	1.1	1.9	,,	0.2	,,	
7	3.0	1.2	1.8	,,	0.2	,,	
8	3.0	1.3	1.7	,,	0.2	,,	Distinct bands were formed.
9	3.0	1.4	1.6	,,	0.2	,,	
10	3.0	0.8	2.2	Na_2HPO_4 (0.5 mol)	0.7	,,	A few bands and a long stopper were formed.
11	3.0	0.8	2.2	,,	0.5	,,	
12	3.0	0.9	2.1	,,	0.5	,,	Irregular bands were formed.
13	3.0	0.6	2.2	,, +Citrate (3%)	0.5 0.2	,,	Very distinct bands were formed.
14	3.0	1.2	1.8	Na_2HPO_4 (0.5 mol)	0.5	,,	Close bands were formed.
15	3.0	0.9	2.1	Phosphate mixture	1.0	,,	A few bands were formed.
16	3.0	1.1	2.1	,,	0.8	,,	
17	3.0	1.3	2.1	,,	0.6	,,	Some indistinct bands were formed.
18	3.0	1.5	2.1	,,	0.4	,,	
19	3.0	1.8	2.1	,,	0.1	,,	No band was formed.
20	3.0	0.9	2.1	$Co(NO_3)_2$ (5%)	0.5	Na_2HPO_4 0.5 mol	A stopper and two bands were formed.

The bands of cobalt phosphate were often irregular. The bands and the large stopper of precipitate were influenced by diurnal cause. In No. 1, five bands consisting of relatively coarse crystals were formed. In No. 2, seven bands were formed, being somewhat irregularly distributed. No. 3–No. 7 gave what seemed to be compound bands of cobalt phosphate and probably of cobalt silicate. In these cases seven or eight rather indistinct bands were formed. In No. 8 and No. 9, the precipitate deposited continuously from the top to the middle part of the gel and eight bands were formed at the bottom. No. 10 gave a stopper 18 mm. long and five bands of relatively coarse crystals. No. 11 gave a stopper of 19 mm. long and three distinct bands consisting of coarse crystals, every band being about 3 mm. thick. In No. 12, five irregular bands were formed. In No. 13, a stopper 18 mm. long and three very distinct bands were formed as shown in Fig. 14. In No. 14, bands were close to each other and a precipitate grew even in the interspaces between bands.

The phosphate mixture, which was used in the experiments of No. 15–No. 19, was a mixture of six volumes of 0.5 mol secondary sodium phosphate and four volumes of 0.5 mol primary potassium phosphate. In this mixture, hydrogen ion concentration was almost the same with that of a neutral solution. The effect of the concentration of inner electrolyte were investigated in these experiments. In No. 15 a stopper and three distinct bands were formed, and in No. 16 a stopper and three bands were obtained. In No. 17 and No. 18 a stopper and four bands were formed, and the crystals were so coarse and so widely scattered, that the bands were very indistinct. No. 19 gave no bands. In No. 20, a stopper of 14 mm. length and two thick bands, 4 mm. and 8 mm. thick respectively, were obtained. The interchange of the inner and the outer electrolyte was possible in this case.

Cobalt Phosphate in Gelatine Gel. The formation of rhythmic bands of cobalt phosphate in silicic acid gel has already been described in a preceding paragraph. The formation of a similar rhythmic precipitate in gelatine was subsequently examined. Five percent solution of cobalt nitrate was poured on a gelatine gel (3%), which was made from purified ash-free gelatine and contained the secondary sodium phosphate as its inner electrolyte. The gel was made by mixing 5.5 c.c. of gelatine solution with 0.5 c.c. of 0.5 mol solution of secondary sodium phosphate. In this case we obtained two imperfect bands consisted of scattered crystals. This result was due to the relatively large acidity of the gel, and to the fact that cobalt phosphate has a considerable solubility in such an acidic gel.

If tertiary sodium phosphate was added to the gel instead of secondary one, a well-developed rhythmic precipitate of cobalt phosphate can be obtained. It seems, from this result, that acidity of the gel was favourable to the formation of rhythmic bands. The right photograph in Fig. 14 shows the rhythmic precipitate of cobalt phosphate in gelatine.

Cobalt Sulphide in Silicic Acid Gel. When a barium sulphide solution diffuses into a gel containing cobalt acetate or nitrate as inner

electrolyte, very close black bands are obtained. Riegel[44] had experimented on this subject, who placed a silicic acid containing sodium sulphide on a solid silicic acid gel containing cobalt nitrate, and obtained the rhythmic bands of cobalt sulphide. In this case, however, the sodium sulphide finally destroys the silicic acid gel. So sodium sulphide is inadequate as an outer electrolyte to obtain this rhythmic precipitate. The present author, therefore, used barium sulphide as the diffusing electrolyte instead of sodium sulphide, and obtained very close but sharp bands. Thus more than 20 bands were often counted in the range of 10 mm. which situated at the depth of 30 to 40 mm. from the top of the gel. The conditions and the results are shown in Table 38.

Table 38.

No.	Gel: Na_2SiO_3 solution (d=1.06) (c.c.)	Gel: CH_3CO_2H solution (c.c.)	Gel: Inner electrolyte (c.c.)	Outer electrolyte	Results
1	3.0	0.75 N 3.0	$Co(NO_3)_2$ (5%) 0.20	Saturated solution of BaS	Close black, distinct bands were formed.
2	3.0	,, 3.0	,, 0.10	,,	
3	3.0	,, 3.0	,, 0.05	,,	
4	3.0	,, 3.0	$Co(NO_3)_2$ (1%) 0.20	,,	
5	3.0	,, 3.0	,, 0.15	,,	
6	3.0	,, 3.0	,, 0.10	,,	No band was formed.
7	3.0	1.0 N 3.0	$Co(NO_3)_2$ (5%) 0.10	,,	Many bands of saturn structure were formed.
8	3.0	0.75 N 3.0	Sat. solution of BaS 0.12	$Co(NO_3)_2$ 5%	Somewhat incomplete banding occurred.
9	3.0	,, 3.0	$Co(NO_3)_2$ (5%) 0.20	Saturated solution of BaS	Close typical bands were formed.
10	3.0	,, 3.0	,, 0.20	3/4 sat. solution of BaS	
11	3.0	,, 3.0	,, 0.20	1/2 sat. solution of BaS	
12	3.0	,, 3.0	,, 0.20	1/4 sat. solution of BaS	

The intervals between the bands became larger with the decrease of the inner electrolyte. In No. 1, the bands were so close that we could scarsely see them even by transmitted light. In the order of No. 2, No. 3, and No. 4, the bands were separated by progressively larger interspaces. The number of bands formed became very small in No. 5, and no bands formed in No. 6. In such a gel of high acidity as in No. 7, the bands were separated from each other and often many bands of saturn structure were formed. The influence of the concentration of outer electrolyte was remarkable. The number of bands between 30 mm. and

(44) Riegel, *J. Phys. Chem.*, **35** (1931), 1675.

60 mm. depths from the surface of the gel was counted in No. 9–No. 12, and obtained 72, 54, 49, and 45 bands in No. 9, No. 10, No. 11 and No. 12 respectively.

The interchange of the inner and outer electrolytes was tried in No. 8. When barium sulphide was dissolved in the gel as an inner electrolyte, rhythmic bands were also obtained. But the bands were not so well-developed as in the case in which the cobalt salt was contained in the gel. In this case diurnal bands were also recognised in the lower part of the gel.

Copper Iodate in Silicic Acid Gel. When copper sulphate solution diffused into silicic acid gel containing potassium iodate as an inner electrolyte, a rhythmic precipitate of copper iodate which was different from an ordinary one, was obtained. The bands often consisted of a bluish white stopper of precipitate, a few bluish white compact bands and one or two diffuse blue bands. The conditions for this rhythmic precipitation are given in Table 39.

Table 39.

No.	Gel				Outer electrolyte	Results
	Na_2SiO_3 solution (d=1.06) (c.c.)	Water (c.c.)	Acid (c.c.)	Inner electrolyte (c.c.)		
1	4.0	1.9	CH_3CO_2H (1 N) 2.4	KIO_3 (5%) 0.2	$CuSO_4$ 2 N	A stopper and a diffuse band was formed.
2	4.0	1.6	,, 2.4	,, 0.5	,, ,,	A stopper and a few bands were formed.
3	4.0	1.3	,, 2.4	,, 0.8	,, ,,	
4	4.0	0.6	,, 2.4	,, 1.5	,, ,,	
5	4.0	0.1	,, 2.4	,, 2.0	,, ,,	
6	3.0	0.9	,, 2.1	,, 1.0	,, ,,	
7	3.0	1.0	,, 2.0	,, 1.0	,, ,,	
8	3.0	1.1	,, 1.9	,, 1.0	,, ,,	
9	3.0	1.2	,, 1.8	,, 1.0	,, ,,	
10	3.0	1.3	,, 1.7	,, 1.0	,, ,,	
11	3.0	1.4	,, 1.6	,, 1.0	,, ,,	
12	3.0	1.5	,, 1.5	,, 1.0	,, ,,	
13	3.0	1.7	,, 1.3	,, 1.0	,, ,,	Many close bluish white bands were formed.
14	4.0		CH_3CO_2H (0.6 N) 4.0	,, 1.0	$CuSO_4$ 2 N	A stopper and a few bands were formed.
15	4.0		,, 4.0	,, 1.0	,, 1.5 N	
16	4.0		,, 4.0	,, 1.0	,, 1.0 N	
17	4.0		,, 4.0	,, 1.0	,, 0.5 N	
18	4.0		,, 4.0	,, 1.0	,, 0.25 N	
19	4.0		HCl (0.7 N) 4.0	,, 1.3	$CuSO_4$ 2 N	No band was formed.

In No. 1, a stopper of 2.5 cm. in length and a faint band were formed. As the concentration of the inner electrolyte was increased, the length

of the stopper decreased and the number of the bands formed increased. In No. 2, a stopper of 2.0 cm. in length, a distinct and compact band and two diffuse bands consisting of scattered spherulites were formed. In No. 3, the length of the stopper was 1.6 cm., and a distinct band and two thick diffuse bands were formed. In No. 4, stopper of 1.4 cm. in length, a sharp band and three spherulite bands were obtained. In No. 5, no stopper was formed and at a depth of 0.8 cm. from the top of the gel a band 0.5 cm. thick, two other sharp bands and two diffuse spherulite bands were formed. The influence of the acidity of the gel was observed in No. 6–No. 13. The stopper was thin or entirely missing in the more acidic gels, while it was thick in the more basic gels. No. 6 gave no stopper but three bands below the depth of 3 mm. from the top of the gel successively and one more far apart from them. Analogous results were obtained in No. 7 and No. 8, though every band was thicker than those of No. 6. Both No. 9 and No. 10 gave a stopper of 1.5 cm. in length and three globular bands. No. 11 gave two sharp and three spherulite bands and a stopper in which two bands were recognised. In No. 12, a thick stopper, in which also two bands were recognised, and two sharp and three diffuse bands were formed. No. 13 gave many bluish white bands but the banding was irregular. No. 14 gave a stopper of 1.6 cm in length and one sharp and two spherulite bands. No. 15 and No. 16 gave analogous results to No. 14 but the stopper was shorter in No. 15 and still shorter in No. 16. In No. 17 a thin stopper and two spherulite bands, and in No. 18 a still thinner stopper and a spherulite band were formed. In a gel which was prepared by mixing a sodium silicate solution ($d = 1.06$) and hydrochloric acid, copper iodate did not form bands. No. 19 showed this result.

In short, the bands become shorter and the number of sharp compact bands increases with the increase of the concentration of inner electrolyte. With the increase of acidity, the stopper becomes thinner. The number of the bands formed becomes larger in the less acidic gels and in such a basic gel as shown in No. 13, many bluish white bands are formed. These bands are a compound rhythmic precipitate of copper iodate accompanying copper hydroxide and copper silicate. The formation of bands becomes difficult with the decrease of the concentration of copper sulphate, as the compact bands turn into a spherulite bands.

Copper Carbonate in Silicic Acid Gel. A rhythmic precipitate of copper carbonate was obtained by the diffusion of copper sulphate solution into a silicic acid gel containing ammonium carbonate. The bands were not so sharp and the upper and lower surfaces of each band seemed diffuse. The intervals between the bands were large and the thickness of every band was also large. An irregular banding was produced in a basic gel. This seemed also to be due to the formation of copper carbonate accompanied by copper hydroxide and copper silicate. In a fairly acidic gel, the carbonate in the gel was decomposed and escaped from it. Concentrated acid is also inadequate to the rhythmic precipitation. The conditions of the experiments are given in Table 40.

In gels of the same acidity, the larger the concentration of the inner electrolyte is, the thicker the stopper becomes. This was seen from

Table 40.

No.	Gel			Outer electrolyte	Results
	Na_2SiO_3 solution (d=1.06) (c c.)	CH_3CO_2H solution (c.c.)	Inner electrolyte (c.c.)		
1	3.0	0.5 N 3.0	$(NH_4)_2CO_3$ (0.5 N) 1.0	$CuSO_4$ 2 N	Irregular bands were formed.
2	3.0	0.6 N 3.0	,, 0.2	,,	
3	3.0	,, 3.0	,, 0.5	,,	Rhythmic bands were formed.
4	3.0	,, 3.0	,, 1.0	,,	
5	3.0	0.73 N 3.0	,, 1.0	,,	
6	3.0	0.75 N 3.0	Na_2CO_3 (5%) 0.3	,,	No band and only a stopper was formed.

No. 2–No. 4. No. 1 gave an irregular banding of bluish white precipitate. No. 2 gave a thin stopper and four bands. In No. 3, a stopper 15 mm. long, two distinct bands, and a faint band were formed. In No. 4, a stopper 17 mm. long, two distinct bands, and two faint bands were formed. In No. 5, three bands which were separated by very large intervals, were formed. Under the same conditions, excepting the acidity of the gel, the stopper was thinner in the more acidic gels. In an acidic gel, the intervals between the bands become larger and the precipitate become greenish. On the other hand, the increase of the concentration of the inner electrolyte tends to shorten the intervals between the bands and change the colour of the bands from greenish blue to bluish white. The most adequate condition for the preparation of a gel for this purpose is attained by mixing a sodium silicate solution (d = 1.06) with an equal volume of 0.60–0.73 N acetic acid.

Silver Carbonate in Gelatine Gel. Silver carbonate forms a rhythmic precipitate in ordinary gelatine, which become more distinct in purified gelatine. The conditions for the banding were studied thoroughly,[45] and the results were partly shown in the preceding paragraphs. The most favourable condition was obtained by superposing a 5% silver nitrate solution to a 2.8% gelatine gel in which as much of sodium carbonate had previously been added as to be 0.2% in concentration. This condition gave the rhythmic precipitate in which the distances between bands were very large and it looked as if white tablets were placed in the test tube. These white bands of silver carbonate were tinged with light yellow with the lapse of days, which became black even by diffused light after a long duration.

As an inner electrolyte ammonium carbonate may also be used. In this case, however, the formed rhythmic precipitate differs a little in appearance from that obtained by sodium carbonate. In addition, it was known that the rhythmic bands were formed with ammonium carbonate

(45) Isemura, *J. Chem. Soc. Japan*, **58** (1937), 629.

in varying the concentration in a considerably wide range. The bands in this case did not take the perfect tablet-like forms as in the case of sodium carbonate, but looked like incomplete net-works or cracked plates.

Silver nitrate may be used as an inner electrolyte. When sodium carbonate solution was poured on the gel containing silver nitrate, bands were not so much manifested and sharp as in the case where silver nitrate was allowed to diffuse. When ammonium carbonate was used as an outer electrolyte, the rhythmic bands were formed which dissolved subsequently in order, and remained the rhythmic cracks.

Silver Arsenite in Gelatine Gel. Silver arsenite does not produce rhythmic bands in a commercial non-dialysed gelatine, while it makes distinct bands in a well dialysed one as in the case of lead iodate. The conditions for the formation were studied thoroughly.[45] The most favourable condition for producing this rhythmic precipitate was as follows. As much of sodium arsenite had been added to 2.0% dialysed gelatine as to be 0.1% in concentration. After the gel set firmly, 5–10% solution of silver nitrate was allowed to diffuse into the gel. In this case a yellow continuous precipitate was formed in the range of about 20 mm. from the top of the gel and many thin and sharply defined bands were formed in a further forward part. This was a very beautiful rhythmic precipitate and sensitive to light, readily changing its colour into dark yellowish green and finally into black by the diffused light.

Contrariwise, silver nitrate may be used as the inner electrolyte. A 10% solution of sodium arsenite was poured on 3% gelatine gel containing silver nitrate at the concentrations of 0.1–1.0%. In this condition, the rhythmic precipitate was always formed. Scarsely any difference was found between the rhythmic precipitate produced by this method and that by diffusion of silver nitrate.

Silver Iodate in Gelatine Gel. It had been reported in a previous communication that the silver iodate make rhythmic precipitate in a well-dialysed gelatine, while it does not, in non-dialysed commercial gelatine.[45] The most favourable condition for producing a rhythmic precipitate of this substance is as follows. A 5% potassium iodate solution was allowed to diffuse into 2.8% gelatine gel, in which as much of silver nitrate had been dissolved as to be 0.1% in concentration. The rhythmic precipitate produced in this case was very peculiar in shape, showing a greatly different form from any rhythmic precipitate which the author had ever seen. That is, one band was a thin disc composed of very fine crystals and an annexed band was above it, which consisted of a small number of extremely fine precipitate. A layer of the same precipitate as one above the thin disc was annexed below. In the lower part, as going downward from it, the precipitated particles became coarse and there was formed a layer of massive particles. These series of layers formed one periodic structure and adjoined the next series across a clear space. The precipitate produced between this thin band and the subsequent one did not originate from the impurities in the gelatine, being different from the so-called secondary bands present between the rhythmic precipitate of silver chromate. It was apparent from the facts

that even though potassium iodate was allowed to diffuse into the dialysed gelatine, which was used for the experiment, no precipitate was produced in the absence of inner electrolyte and the band of coarse particles between two successive bands was always only one. Fig. 6 shows an example of this rhythmic precipitate.

In experiment as to whether silver iodate could produce the rhythmic precipitate, the author employed at first, reversely to the above mentioned method, silver nitrate as the diffusing agent and potassium iodate as the inner electrolyte. In this case, the rhythmic bands of utterly different kind from the above mentioned was obtained. The particles of thus obtained rhythmic precipitate was coarse and did not gather close into a tablet-like band. The bands were coarse and uneven, so that they were inevitably indistinct. In addition, scarsely any clear spaces between successive bands was observed. Fig. 5 shows this type of the bands.

Silver Capronate in Gelatine Gel. Silver capronate forms a well defined rhythmic precipitate in gelatine jelly. Well dialysed gelatine, freed from chlorides and phosphates, was dispersed into 4% sol, the acid was added and then allowed to set. The concentration of the acid was 0.05–0.1 mol. per litre. After the gel set firmly, 20% silver nitrate solution was poured on it. White thin bands with relatively large distances were obtained.

Silver Phosphate in Silicic Acid Gel. When a silver nitrate solution was allowed to diffuse into a silicic acid gel which contained sodium phosphate, rhythmic precipitate of silver phosphate was obtainable if the acidity of the gel was adequate to the reaction. In a gel of low acidity, silver silicate would probably have formed accompanying the silver phosphate and yellowish brown close bands were formed. The conditions for the experiments are shown in Table 41.

Table 41.

No.	Gel				Outer electrolyte	Results
	Na_2SiO_3 solution (d=1.06) (c.c.)	Water (c.c.)	CH_3CO_2H (1 N) (c.c.)	Inner electrolyte (c.c.)		
1	3.0	0.8	2.2	Na_2HPO_4 0.3 (8.4%)	$AgNO_3$ 10%	Typical rhythmic precipitate was formed.
2	3.0	0.8	2.2	,, 0.3	$AgNO_3$ 5%	Rhythmic bands were formed.
3	3.0	0.9	2.1	,, 0.3	,, ,,	
4	3.0	1.0	2.0	,, 0.3	,, ,,	
5	3.0	1.1	1.9	,, 0.3	,, ,,	Bands were formed and below bands crystals were scattered about.
6	3.0	1.2	1.8	,, 0.3	,, ,,	
7	3.0	1.3	1.7	,, 0.3	,, ,,	
8	3.0	1.4	1.6	,, 0.3	,, ,,	
9	3.0	1.5	1.5	,, 0.3	,, ,,	Faint bands were formed.

In No. 1, well-developed yellow bands of silver phosphate were formed. In No. 2 and No. 3, seven or eight bands consisting of relatively coarse crystals were formed at the top of the gel and below the last formed band crystals were scattered. In No. 4, the best rhythmic bands were obtained. In a gel which was less acidic, silver silicate would probably have formed accompanying silver phosphate. The bands were closer, and in the lower part of the gel, crystals were coarse and no band was recognisable. No. 5 and No. 6 are the cases. In No. 7 and No. 8, finer close yellowish brown bands were formed, consisting probably of silver phosphate and silicate. No. 9 was inadequate to the banding, for, in this case only faint bands were formed at the top of the gel, and below these there was spread the precipitate uniformly. In short, the conditions from No. 1 to No. 4 were favourable to form a rhythmic precipitate of silver phosphate in a silicic acid gel.

Silver Arsenate in Silicic Acid Gel. It is expected that silver arsenate forms rhythmic precipitate in silicic acid gel, by the analogy of silver phosphate. Silver arsenate bands in gelatine gel was already reported by Rayleigh.[46] The present author has examined on this substance in silicic acid gel. A sodium arsenate solution (0.3 c.c. of 10% solution) was added to a sol which was prepared by mixing 3.0 c.c. of a water glass solution ($d = 1.06$) with an equal volume of 0.6–0.75 N acetic acid. After the sol set firmly to a gel, 5 or 10% solution of silver nitrate was poured on the gel and let diffuse in it. A chocolate brown precipitate deposited rhythmically. The bands were in contact with each other at the top of the gel, while at the bottom of the gel they were distinct and separated by marked gaps. In an ordinary room, the silver salt was decomposed by light and the rhythmic precipitate was blackened, so this experiment was favourably conducted in a dark room.

Silver Iodate in Silicic Acid Gel. The formation of a rhythmic precipitate of silver iodate in a gelatine jelly was already reported in a preceding paragraph. Now, its formation in a silicic acid gel will be described. By the diffusion of silver nitrate into a silicic acid gel containing potassium iodate as inner electrolyte, somewhat curious white bands consisting of flocculent clusters of relatively coarse crystals were formed. As the diffusion proceeded down, the crystals became coarser and accordingly each of the flocks which formed the bands grew considerably large and the bands became indistinct and uneven. We could see, however that the precipitate had the nature of bands, from the fact that the bands separated by marked interspaces by the addition of a small quantity of citrate to the gel. The conditions for the experiments are summarised in Table 42.

No. 1 and No. 2 gave such bands as described above. About 40 bands were formed within 50 mm. from the surface of gel. In No. 3, no band but yellow precipitate was formed at the top of the gel, which was probably silver iodate accompanying silver silicate, while in the lower part of the gel complicated yellow bands were formed. In No. 4,

(46) Rayleigh, *Phil. Mag.*, **38** (1919), 738.

Table 42.

No.	Gel				Outer electrolyte	Results
	Na_2SiO_3 solution (d=1.06) (c.c.)	CH_3CO_2H solution (c c.)	Inner electrolyte (c.c.)			
1	3.0	0.75 N 3.0	KIO_3 (5%)	0.65	$AgNO_3$ (5%)	Rhythmic bands were formed.
2	3.0	0.70 N 3.0	,,	0.65	,,	
3	3.0	0.60 N 3.0	,,	0.65	,,	Irregular banding occurred.
4	3.0	0.50 N 3.0	,,	0.65	,,	No band was formed.
5	3.0	0.75 N 3.0	,, +citrate (3%)	0.65 0.3	,,	Most distinct bands were formed.
6	3.0	0.75 N 3.0	KIO_3 (5%)+ aconitate (1.5%)	0.65 0.3	,,	Distinct bands were formed.
7	3.0	0.50 N 3.0	KIO_3 (5%)	0.65	,,	Irregular bands were formed.

however, a yellow precipitate was formed from the top to the bottom of the gel, and no band was recognisable. As it was already stated, the presence of a small quantity of citrate in the gel favours the formation of these rhythmic bands. In No. 5, the best bands were obtained. Each band consisted of many floculent clusters of crystals separated by marked gaps. The effect of aconitate in making the crystals small is less than that of citrate. In No. 6, the bands were less distinct than in No. 5. In No. 7, a result analogous to No. 3 was obtained.

In a gelatine jelly, when the inner electrolyte was interchanged with the outer electrolyte, that is to say, by the diffusion of potassium iodate into a gel containing silver nitrate, a rhythmic precipitate of an entirely different appearance was formed. In a silicic acid gel, however we cannot dissolve silver nitrate, because it reacts with silicic acid and precipitation occurs. So the interchange of the electrolytes is impossible in a silicic acid gel.

Calcium Phosphate in Silicic Acid Gel. Several reports have already published in regard to the formation of rhythmic precipitate of calcium phosphate in other medium than the silicic acid gel. But the banding in the silicic acid gel have never been reported. The present author therefore has tried an experiment in order to know whether the Liesegang phenomenon of calcium phosphate could be caused or not in the silicic acid gel.[16] And it was certified that calcium phosphate produced an extremely prominent rhythmic precipitate even in the silicic acid gel, and that the banding was closely related to the hydrogen ion concentration of the medium. The results were partly described in the preceding part of this paper.

The following is one of the most favourable conditions. That is, for dissolving phosphate in the gel, 1 c.c. of a 8% solution of secondary

sodium phosphate was added to 10 c.c. of a 0.75 N acetic acid and then 10 c.c. of a solution of sodium silicate ($d = 1.06$) was added to it and allowed to stand to gelatinise. After the gel set firmly, 2 mol solution of calcium nitrate was superposed on it.

For dissolving calcium salt in the gel, after a sodium silicate solution ($d = 1.06$) was mixed with 10 c.c. of 0.75 N acetic acid and 1.0 c.c. of a 10% calcium chloride solution was added to the mixture, while stirring up. After the gel set firmly, 8% secondary sodium phosphate was poured on it. White sharp bands were formed in both cases spacing regular intervals.

Calcium Oxalate in Silicic Acid Gel. Calcium oxalate forms a rhythmic precipitate in silicic acid gel. The adequate condition for the banding is as follows: To 5 c.c. of sodium silicate solution ($d = 1.06$) add 5 c.c. of a mixture of acetic acid and oxalic acid (0.5 N, ratio of the two acids; 1:1 or 1:3). The silicic acid gel set in one night. Then ca. 5 c.c. of calcium chloride solution (10–25% solution) are poured on the gel. The rhythmic bands are formed which has an appearance like an opal. Clear spaces between bands are so narrow that the bands can better be seen by the transmitted light. Too large or too small quantity of oxalic acid prevents the formation of calcium oxalate bands.

Strontium Oxalate in Silicic Acid Gel. Strontium oxalate forms a rhythmic precipitate in silicic acid gel in the presence of potassium citrate as the third substance. The condition for the banding is as follows: To 5 c.c. of sodium silicate solution ($d = 1.06$) add equal volume of the mixed acid above described and 0.01–0.02 g of potassium citrate. After setting the gel, put 5 c.c. of 25% strontium nitrate solution on it. About a week later, the formation of bands is observed by the transmitted light. Citrate accelerates, in this case, the formation of nucleus of the crystals. No strata were formed when no citrate was added in the gel. The nucleus formation is accelerated by the presence of the citrate and accordingly the formation of strata will become easier. The author found the formation of dense, white bands of strontium oxalate by adding a small quantity of citrate to the mixture before setting.

Nickel Dimethylglyoxime in Silicic Acid Gel. When an alcoholic solution of dimethylglyoxime is added to a solution of nickel salt, a red voluminous precipitate of nickel dimethylglyoxime is produced. Such a complex compound forms also rhythmic bands in a silicic acid gel.[47] Five cubic centimeters of a solution of sodium silicate ($d = 1.06$), was taken into test tube and mixed with 5 c.c. of 1 N acetic acid and then 0.25 c.c. of a saturated solution of dimethylglyoxime in alcohol was added to it and the mixture was left quiet until it set. A 15% solution of nickel sulphate was poured on the gel. Red rhythmic precipitate was formed which consisted of dendrites of fine crystals.

If the used quantity of dimethylglyoxime was smaller than 0.1 c.c. the precipitate was so coarse that no bands were produced. If the

(47) Isemura, *J. Chem. Soc. Japan*, **57** (1936), 546.

quantity was larger than 0.5 c.c., the bands were so dense that the formation of a rhythmic precipitate was rather indistinct. .If the solution of nickel sulphate was smaller than 7.5% in concentration, the formed bands were smaller in number and the crystals of nickel dimethylglyoxime became coarse, so that the bands blurred. The adequate concentration of nickel sulphate, therefore, should be 10–20%. The formation of bands of this precipitate was strongly affected by the hydrogen ion concentration of the medium. The most adequate *p*H value for the formation of this rhythmic precipitate was about 5.0–5.5.

Lead Chromate in Silicic Acid Gel. It has generally been considered that the lead chromate forms bands in agar-agar gel but not in silicic acid gel. But the author has obtained the rhythmic bands of this substance in silicic acid gel by modifying the conditions appropriately. It is doubtful, however, whether the bands obtained in this case are the Liesegang phenomenon or not. They are probably the diurnal bands. The condition of the banding is as follows: In 5 c.c. of sodium silicate solution ($d = 1.06$) dissolve 0.01–0.005 g. of potassium chromate as inner electrolyte and 0.03–0.05 g. of glucose. To this solution add an equal volume of a half normal solution of acetic acid. After setting, 10% lead nitrate solution is superposed on the gel as outer electrolyte. Ten or more days later, it was obserbed that many thin and crowded bands were formed. If too much potassium chromate was added, the dendrites were also formed simultaneously, and if too little, the bands became very vague.

H. N. Holmes[34] has found, in the periodic precipitate of mercuric iodide in silicic acid gel, that the presence of glucose in the gel makes the bands very much sharper. The author has found, in the same manner, that the addition of glucose makes the periodic structure of the lead chromate much charper. In this case, two periodicities exist just as the case of silver chromate banding in gelatine containing small amount of soluble chlorides and phosphates. Larger periodicity is easily recognised while smaller one is often difficult to observe without a magnifying glass. At the lower part of the tube, however, both can easily be recognised with the naked eyes. It is interesting that in this case the upper part of the jelly is coloured yellow, the subsequent layer, orange, and the lower, brown. The banding appears under this part and becomes yellow again at the lowermost part. It seems that such a colour change is caused by the difference of the size of formed crystals.

Lead Iodide in Silicic Acid Gel. When potassium iodide solution diffuses into silicic acid gel containing lead acetate, fern-like fronds grow down in the gel, mixing with hexagonal plates. It is believed that the lead iodide does not form rhythmic precipitate in the silicic acid gel. But it was found, in rare cases, that the rhythmic precipitate of this substance occurred accidentally. The author studied the condition under which the rhythmic precipitates are formed,[12] and found that when the crystals become relatively small, the rhythmic precipitates are generally formed. The increase of the inner and outer electrolyte is favourable to the formation of small crystals. A third substance must be added which makes the crystals of lead iodide small in order to make sure

the formation of rhythmic bands. Citrate and tartrate are fit to this purpose as already mentioned in the preceding paragraph. One normal acetic acid containing 0.9 c.c. of 1 N lead acetate and 0.55 c.c. of 3% potassium citrate to every 10 c.c. was mixed with the equal volume of water glass solution ($d = 1.06$) and poured into a test tube. After the silicic acid had set firmly, it was covered with 2 N potassium iodide solution. By this procedure good rhythmic bands from fine crystals were always formed. Similarly, to make the gel, 1 N acetic acid containing 1.2 c.c. of 1 N lead acetate and 0.8 c.c. of 3% tartaric acid to every 10 c.c. was mixed with the water glass solution. Then the gel was covered with 2 N potassium iodide solution. Beautiful well-defined rhythmic precipitates consisting of relatively large crystals were produced. These results show that the formation of bands is the true Liesegang's phenomenon. But the crystallisation of lead iodide is much influenced by the temperature and the light. The crystallisation of this substance is faster in day time than in night. Moreover, lead iodide is decomposed by bright light, especially in the presence of citrate and the colour of crystals changes to black. For these reasons, two other periodic deposition of diurnal nature, which are caused by the change of temperature and light, are produced as the reflex of the external periodicities. Frequently, these three rhythms, Liesegang's and two diurnal bandings, appear at the same time in one test tube and the complicated bands are obtained.

Lead Iodate in Gelatine Gel. As already mentioned, lead iodate is hardly obtained as rhythmic precipitate in non-dialysed gelatine. Because the rhythmic bands of lead iodate becomes undistinguishable by a continuous, white precipitate probably consisting of chloride and phosphate of lead in ordinary commercial gelatine, which contains always some impurities of chloride and phosphate. Very beautiful and well-defined rhythmic precipitate is formed by using the gelatine purified by electrodialysis or by Loeb's method.[48] One of the most favourable conditions for the banding is as follows: a 0.5 mol solution of lead acetate was allowed to diffuse into a 2% purified gelatine gel containing as much of potassium iodate as to be 4% in concentration. This rhythmic precipitate is one of the most distinct and beautiful example which the author have ever seen. Lead iodate makes often the helicoidal precipitate. The reason for the formation of helicoidal precipitate is not thoroughly clear but probably it is ascribed to the deformation of gel by the pouring of diffusing electrolyte on it. The conditions for the banding and the effect of various influences were studied and the results were partly shown in the preceding paragraphs. Light has no influences on this rhythmic precipitate and the ageing of gel also has no influences.

Lead Iodate in Silicic Acid Gel. It was already reported in the preceding paragraph, that if lead acetate diffuse into a gelatine gel containing potassium iodate, a very beautiful well-defined rhythmic precipitate is formed. But on standing this rhythmic precipitate for a long time, more lead acetate diffuse into the gel, reacts with the already formed

(48) Isemura, *J. Chem. Soc. Japan*, **58** (1937), 301.

lead iodate, and transforms the bands into those consisting of large crystals. It seems that the band of coarse crystals are composed of a double salt of relatively high solubility. This transformation from fine well-defined bands to incomplete bands of coarse crystals is far faster in silicic acid gel than in gelatine. The bands were scarsely observed in silicic acid gel after the transformation, because the crystals formed were large scattered globules. The quick transformation is probably due to the lack of protective action of the silicic acid gel. Six c.c. of a sol which was prepared by mixing equal volumes of a sodium silicate solution ($d = 1.06$) and 0.70–0.75 N acetic acid solution is added with 0.6 c.c. of 5% potassium iodate solution. After the gel set firmly, a lead acetate solution (1 N) was poured on the gel. About ten bands were formed after 24 hours but these transformed, successively, from the top, into bands consisting of large globules, which blurred within two or three days.

Lead Phosphate in Silicic Acid Gel. It was examined whether lead phosphate was precipitated in rhythmic bands or not in silicic acid gel. A sol which was prepared by mixing 3.0 c.c. of a ($d = 1.06$) solution water glass with an equal volume of 0.75 N acetic acid, is added with 0.5 c.c. of a 0.5 mol solution of sodium phosphate. After the sol set firmly to a gel, 1 N solution of lead acetate or lead nitrate was superposed on the gel. The banding was indistinct. Somewhat long needles were formed and it seems that these needles distribute to make faint bands. When 0.3 c.c. of a 3% potassium citrate solution was added beforehand to the gel, distinct rhythmic bands were formed. When a lead acetate solution (1 N) diffused into the gel, more than twenty bands were recognised. But in the case of the diffusion of lead nitrate, the bands were often imperfect and consisted of fragments.

Lead Phosphate in Gelatine Gel. The lead phosphate precipitates in silicic acid gel as somewhat long needles and the rhythmic nature of this precipitate is, as already mentioned, indistinct. In the presence of a small quantity of citrate, however, the crystals became smaller and they appeared as a rhythmic precipitate. It is known that crystals formed in gelatine are generally smaller than those formed in a silicic acid gel. So, it is expected that lead phosphate forms rhythmic bands in gelatine. The author made an experiment on it. Sodium phosphate (0.5 c.c. of 0.5 mol solution) was dissolved in 6 c.c. of a 3% solution of purified ash-free gelatine. After the gel set firmly, 1 N solution of lead acetate was poured on the gel as the outer electrolyte. Seven white bands were formed and then the crystals deposited uniformly below these bands.

Cerium Iodate in Silicic Acid Gel. The bands of cerium iodate were obtained by the diffusion of cerium nitrate into silicic acid gel containing potassium iodate as inner electrolyte. The condition for the banding was as follows. A sol which was prepared by mixing 3.0 c.c. of a water glass solution ($d = 1.06$) with an equal volume of 0.7 N acetic acid was added with 1.0 c.c. of a saturated solution of potassium iodate. After the sol set firmly to the gel, 5% solution of cerium nitrate was superposed on it. White beautiful bands were obtained. Every band formed close to each

other. For the first 2.5 cm. from the top of the gel, a continuous white precipitate was formed and for the next 2.5 cm. 15 bands were recognised, separated by narrow clear gaps.

Silver Ferrocyanide in Silicic Acid Gel. A rhythmic precipitate of silver ferrocyanide was obtained by the diffusion of silver nitrate into silicic acid gel containing potassium ferrocyanide. The bands were very close to each other. More than 15 bands were often formed in one centimeter. This banding was already studied by Mukherjee and Chatterji.[49] They concluded that the intervals between bands become smaller with the advance of diffusion. But in the present experiments all of the bands were separated by almost equal intervals. It is doubtful that these bands were formed as a Liesegang phenomenon. This banding is influenced by the acidity of the gel. Some conditions and the results obtained are given in Table 43 and follows.

Table 43.

No.	Gel				Outer electrolyte (5%)	Results
	Na_2SiO_3 solution (d=1.06) (c.c.)	CH_3CO_2H solution (c.c.)		Inner electrolyte (c.c.)		
1	3.0	0.6 N	3.0	$K_4Fe(CN)_6$ (2%) 0.3	$AgNO_3$	A yellow continuous precipitate was formed.
2	3.0	0.7 N	3.0	,, 0.3	,,	A grey continuous precipitate was formed.
3	3.0	0.8 N	3.0	,, 0.3	,,	Close rhythmic bands were formed.
4	3.0	0.9 N	3.0	,, 0.3	,,	
5	3.0	1.0 N	3.0	,, 0.3	,,	
6	3.0	1.0 N	3.0	,, 0.7	,,	

In a gel of low acidity such as No. 1, yellow precipitate was formed uniformly and no band was recognised. In No. 2, also, no band was formed but a white precipitate formed uniformly. In No. 3–No. 5 many close bands were obtained. These bands were type of sub-class II (class II of Chatterji). Generally, the intervals between bands were large in a gel of high acidity. In No. 5, the intervals between bands were larger than those in No. 3 and in No. 4. In No. 6, the bands were very close to each other owing to the relatively high concentration of the inner electrolyte.

Ferric Ferrocyanide in Silicic Acid Gel. Rhythmic bands of ferric ferrocyanide were obtained by the diffusion of ferric chloride into silicic acid gel containing potassium ferrocyanide as an inner electrolyte. These rhythmic bands were indistinct, showing a blue continuous precipitate by reflected light but many bands were seen by transmitted light. The banding was sub-class II type (class II type of Chatterji). The conditions are given in Table 44.

(49) Mukherjee and Chatterji, *Kolloid-Z.*, **50** (1930), 147.

Table 44.

No.	Gel			Outer electrolyte	Results
	Na_2SiO_3 solution (d=1.06) (c.c.)	CH_3CO_2H solution (c c.)	Inner electrolyte (c.c.)		
1	3.0	0.5 N 3.0	$K_4Fe(CN)_6$ 0 1 (2%)	$FeCl_3$ 5%	Faint bands were formed.
2	3.0	,, 3.0	,, 0.3	,,	
3	3.0	1.0 N 3.0	,, 0.1	,,	No band and only a stopper was formed.
4	3.0	,, 3.0	,, 0.3	,,	
5	3.0	,, 3.0	,, 0.7	,,	
6	3.0	0.6 N 3.0	,, 0.3	,,	Blue rhythmic precipitate was observed by transmitted light.
7	3.0	0.7 N 3.0	,, 0.3	,,	
8	3.0	0.8 N 3.0	,, 0.3	,,	
9	3.0	0.9 N 3.0	,, 0.3	,,	
10	3.0	0.8 N 3.0	,, 0.1	,,	No band was formed.

When the concentration of potassium ferrocyanide was small, either the banding was indistinct or no band was formed as in the cases of No. 1, No. 3, and No. 4. In No. 2, brown bands were formed which were thinner in the lower part and separated by small interspaces. These were probably diurnal bands of ferric basic chloride or ferric hydroxide. At the bottom of the gel some rhythmic bands of prussian blue were formed. No. 3 gave no band and only a brown stopper. In No. 4, many blue bands were observed by transmitted light but no band by reflected light. No. 5 gave brown diurnal bands but blue bands were not observed even by transmitted light for the precipitation was too dense. In No. 6–No. 9 blue rhythmic bands were well observed by transmitted light. No. 10 gave no band. A brown band was always observed at the top of the gel in these banded precipitates. These were probably formed by basic chloride of iron, ferric hydroxide or basic ferric acetate which was produced by the hydrolysis of ferric chloride or its interaction with acetic acid. These brown bands were formed simultaneously with bands of prussian blue, and were affected by external rhythms. So the banding was always very irregular. Moreover, this rhythmic precipitate was affected by the acidity of the gel. In a gel of high acidity, many bands were formed in the lower part of the gel, situating close to each other. This was probably due to the fact that the diffusing ferric chloride was not easily hydrolysable in the more acidic gels and so the consumption of ferric chloride by hydrolysis was small. Accordingly, ferric chloride of the same concentration acts as if it were a cencentrated solution in the more acidic gels.

Uranyl Phosphate in Silicic Acid Gel. A rhythmic precipitate of uranyl phosphate was obtained by the action of uranyl acetate with soluble phosphate in silicic acid gel. A sol which was prepared by mixing 3.0 c.c. of a water glass solution (d =1.06) with an equal volume of 0.75 N acetic acid was added with 0.3 c.c. of a 8.74% solution of sodium phosphate. After the gel set firmly, 2% solution of uranyl acetate was superposed on it. Pale yellow bands consisting of relatively coarse crystals were formed. The appearance was entirely analogous to the

bands of uranyl arsenate which will be described later. Coarse crystals have been deposited under the last band. The bands belong to the category of the type of sub-class II.

Uranyl Arsenate in Silicic Acid Gel. The precipitating reaction of uranyl arsenate is analogous to the case of uranyl phosphate. So the formation of rhythmic precipitate of uranyl arsenate in a silicic acid gel was experimented, and a similar result was obtained. A sol which was prepared by mixing 3.0 c.c. of a water glass solution ($d = 1.06$) with an equal volume of 0.75 N acetic acid was added with 0.3 c.c. of a 10% solution of sodium arsenate. After the gel set firmly, 2% solution of uranyl arsenate was superposed on it. Several bands of pale yellow uranyl arsenate were obtained. The crystals forming the bands became coarse with the advance of diffusion. Almost no crystals formed below the last band. These bands were also the sub-class II type.

Summary.

(1) The conditions of the formation of various examples of rhythmic precipitates have been studied. The effects were tested of the change of species and concentrations of gel, inner electrolyte and outer electrolyte, the temperature, the light intensity and the hydrogen ion concentrations of medium and outer electrolyte solution.

(2) The regularity of spacing between bands has been studied. The distance between bands is expressed empirically by the quadratic equation concerning the ordinal number of it. The same equation was deduced from a theoretical standpoint, the physical meaning of the equation being considered.

(3) Classification of the rhythmic precipitates by the cause of formation and by the structure has been proposed. Secondary bands were investigated and discussed.

(4) New examples of rhythmic precipitate have been described, i.e. barium chromate, cobalt phosphate, lead carbonate, lead phosphate, lead iodate, silver arsenate, silver carbonate, silver iodate and silver capronate in gelatine gel, and bismuth chromate, bismuthyl chloride, bismuthyl nitrate, cobalt phosphate, cobalt sulphide, copper carbonate, copper iodate, cerium iodate, calcium phosphate, calcium oxalate, strontium oxalate, ferric ferrocyanide, lead carbonate, lead iodate, lead phosphate, nickel dimethylglyoxime, silver arsenate, silver ferrocyanide, silver phosphate, silver iodate, uranyl phosphate and uranyl arsenate in silicic acid gel. The conditions for the formation of these rhythmic precipitates have been thoroughly investigated.

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Kochi High School, Kochi
and
Chemical Institute, Faculty of Science,
Tokyo Imperial University, Tokyo.

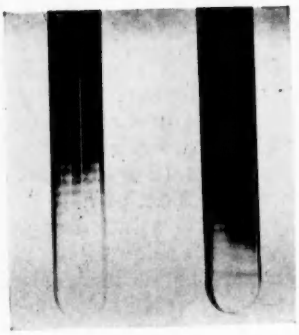

Fig. 1.

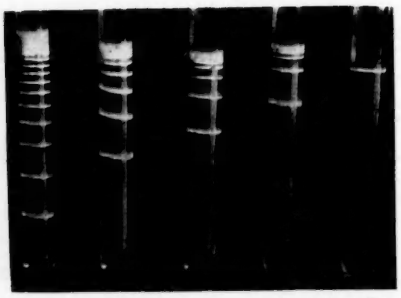

Fig. 2. Na_2CO_3(conc.) → Na_2CO_3 (dil.)

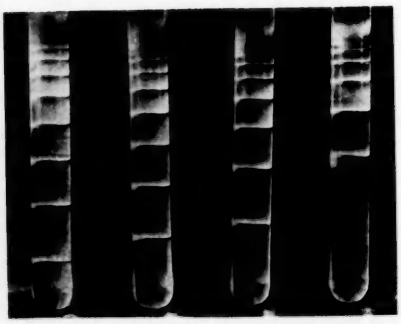

Fig. 3. $AgNO_3$ (conc.) → $AgNO_3$ (dil.)

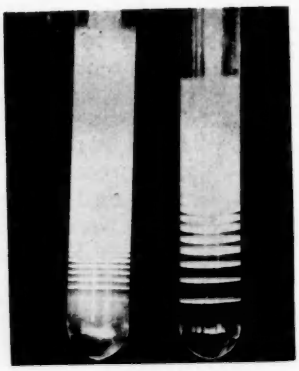

Fig. 4.

Fig. 5.

Fig. 6.

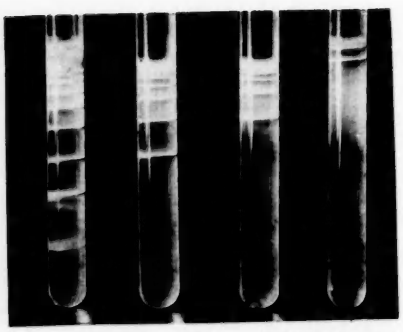

Fig. 7. Gelatine (dil.) → Gelatine (conc.)

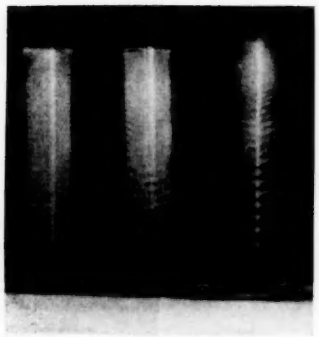

Fig. 8.

Fig. 9.

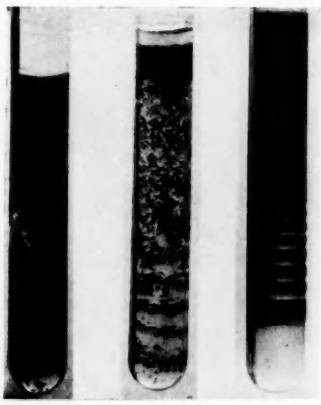

Fig. 10.

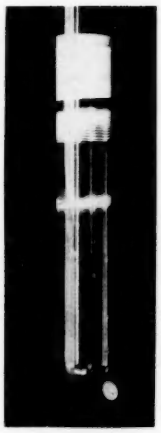

Fig. 11.

Fig. 13.

Fig. 12.

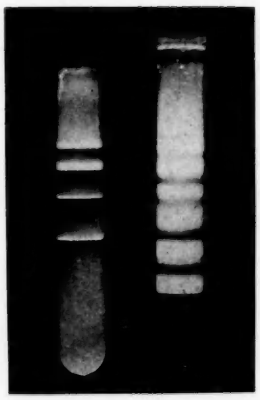

Fig. 14.